

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

# Deliverable D7.1

## Interim report on environmental assessment according to Life Cycle Analysis and REACH methods.

WP 7 – Impact analysis

Version 01

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## Revision History

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## 1 Introduction

Traditionally, environmental science has subscribed to the belief that cement industry is energy and emission intensive. A transition towards deep decarbonisation of these industries is essential [1]. At this respect, CO<sub>2</sub> from the flue gases of a rotary kiln in a cement industry (CO<sub>2</sub>: 25 vol%) could be used for the production of value-added chemicals (acid additives for cement formulations) and materials (CaCO<sub>3</sub> nanoparticles to be used as concrete fillers). In RECODE, the CO<sub>2</sub> produced by cement manufacturing is re-used in a significant part within the plant itself to produce better cement-related products entailing less energy intensity and related CO<sub>2</sub> emissions by a quadratic effect. With this approach, the RECODE project enables a circular-economy system. Its overall sustainability should be yet assessed.

Life cycle assessment (LCA) has been widely adopted to evaluate the potential environmental impacts or drawbacks of products and processes. Therefore, the environmental sustainability of these cement-derived CO<sub>2</sub> utilisation processes will be evaluated by POLITO using the LCA methodology. The entire life cycle of the process will be assessed, encompassing raw materials collection, gas upgrading and purification and final processing through the RECODE concept. The procedure will compare a standard production process with the one implemented in RECODE to evaluate the influence of the RECODE manufacturing routes on the environmental impact of the cement industries. The analyses will be performed according to the ISO 14040/44 normative[2], [3] (cradle-to-gate perimeter). The environmental impacts are selected considering the CML 2001 method[4].

The aim of this Deliverable is to collect the preliminary data derived from the technical Work Packages, in order to create an appropriate Life Cycle Inventory for the LCA modelling. Furthermore, in this Deliverable, POLITO will carry out an interim calculation of the environmental impacts of the RECODE project. The present Deliverable is within the Task 7.1: Environmental impact, which systematically will review the technical data from partners, adapting the Life Cycle Inventory and aiming to provide a final LCA at the end of the project (Deliverable 7.7. Month 48).

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.

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## 2 Life Cycle Assessment

The increased consciousness about the environmental protection, and the possible impacts associated with products and processes has increased interest in the development of methods to better understand and address these impacts. One of the techniques being developed for this purpose is Life Cycle Assessment (LCA). Life Cycle Assessment is a tool to assess the environmental impacts throughout a product life cycle and LCA methodologies are broadly accepted by the scientific community.

LCA addresses the environmental aspects and potential environmental impacts. According to ISO 14040/44 standards, four phases are identified in an LCA study:


- a) Goal and scope definition.
- b) Inventory analysis.
- c) Impact assessment.
- d) Interpretation.

### 2.1 Goal and scope definition

The scope, including system boundary and level of detail, of an LCA depends on the subject and the intended use of the study.

The objectives of this research are to collect information from the partners in order to construct an interim Life Cycle Inventory and to determine the environmental impacts of those RECODE added-value products with properly information already available. Emphasis will be placed on evaluating the greenhouse gases emissions (GHG) that impact to the climate change.

A thorough LCA studies task is foreseen for the entire duration of the project as Task 7.1. This will fill the gap in the literature on the key technology components as well as in the overall process (from CO<sub>2</sub> capture to the production of the cement additives), as well as in single possible critical elements. It is necessary to evaluate the feasibility of the CO<sub>2</sub> utilisation technologies to produce added-value products in an environmental point of view. In this respect, this study takes the cradle-to-gate approach as the system boundaries.

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## 2.2 Life Cycle Inventory (LCI).

The life cycle inventory analysis phase (LCI phase) is the second phase of LCA. It is an inventory of input/output data with regard to the system being studied. It involves the collection of the data necessary to meet the goals of the defined study. Typically, inventory data include raw materials, energy consumption, emissions to atmosphere, water and soil, and the emission of solid, liquid and gaseous wastes.

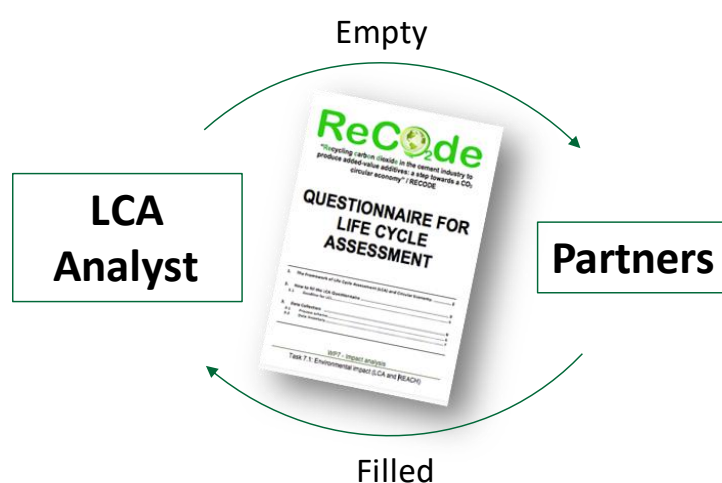



Figure 1. Process for collecting LCA information in order to create an accurate LCA.

An LCA Questionnaire was created and sent to the partners (Figure 1). The Questionnaire is needed to complete the LCI phase. It consists in gathering all the necessary information and data to successfully perform the assessment, including all steps and co-products. The task addressed by LCA inventory could be very time-consuming and intrinsically depend on the data accuracy, considering that this step deeply influences the whole LCA study. POLITO collects the process data from the RECODE partners. The interactions between the partners and the LCA analyst should be frequent in order to update the LCA model as accurate as possible with the new developments in the technical units of the project.

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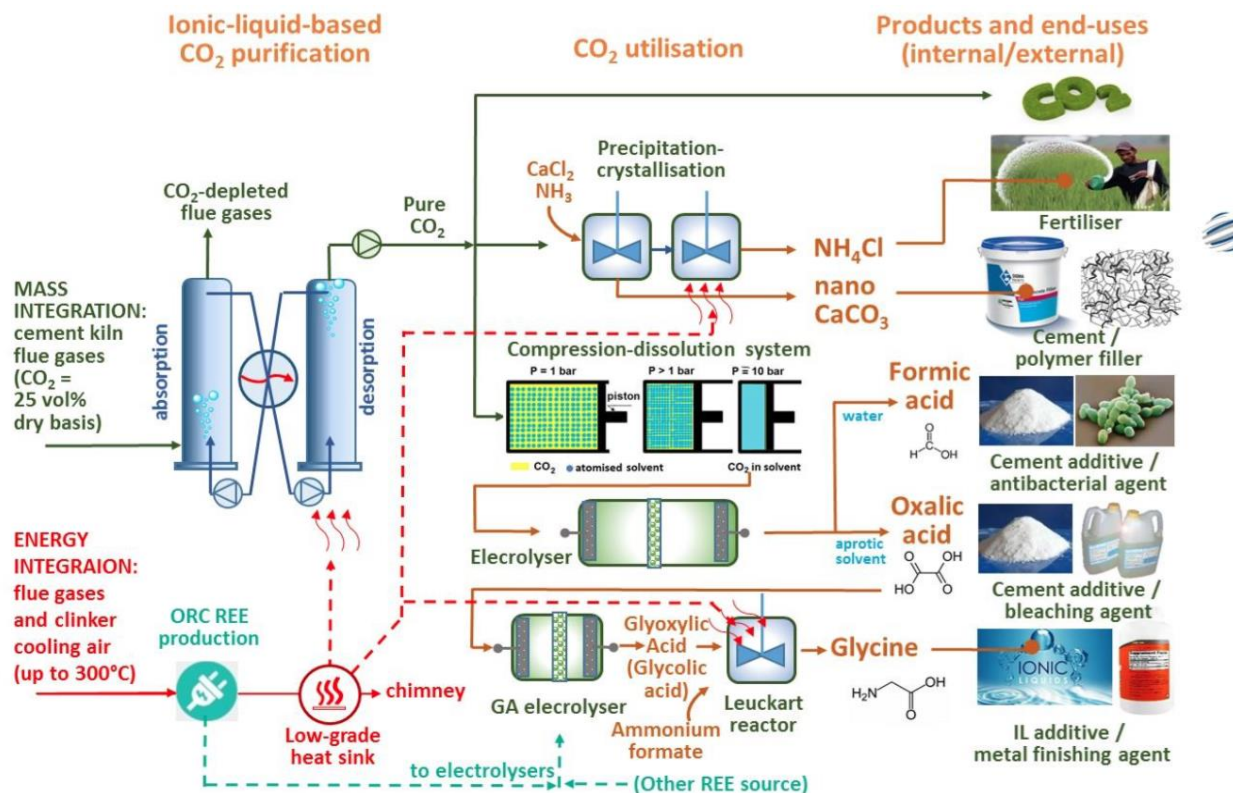


Figure 2. General scheme of RECODE processes.

Figure 2 shows the general scheme of all the processes involved in the RECODE project. With this scheme and the information from the Questionnaires the interim Life Cycle Inventory has been created.

### 2.2.1 Absorption and desorption unit LCI.

The process consists of different gas-treating operations with the aim to supply 97% grade CO<sub>2</sub> to subsequent synthesis units. The main operation is the ionic liquid-based absorption of the CO<sub>2</sub> from the cement plant flue gas. Figure 3 shows a schematic flowchart of the inputs and outputs involved in this unit.

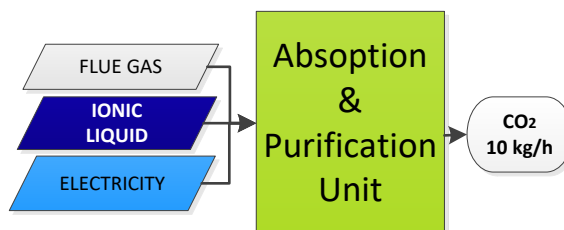



Figure 3. Flowchart of the absorption and purification unit.



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*Table 1. LCI of the Absorption and Purification Unit.*

<b>Outputs</b>		
CO <sub>2</sub> 97%	10	kg/h
<b>Inputs</b>		
Electricity	5.1	kWh
Ionic Liquid	0.11	kg/h
<b>Emissions to air</b>		
Carbon dioxide	-10	kg/h

The separation and recovery of CO<sub>2</sub> is carried out with ionic liquids, through an absorption column and a stripping column. As summarised in Table 1, the absorption and desorption plant produces 10 kg/h of CO<sub>2</sub> captured directly from the flue gas. This plant needs 0.11 kg/h of ionic liquid. So far, RECODE partners have estimated the electricity consumption as 1 kWh/Sm<sup>3</sup> of CO<sub>2</sub> recovered, which includes the consumption of a vacuum group, a chiller, a blower and two pumps. There is still an open discussion between the partners about the consumption of the vacuum group. In the final LCA, it could be a new approach by the fact of putting two vacuum groups in series could consume lower amount of energy. At this point of the project, LCA team decided to take this assumption as the maximum expected. In next updates of the LCA model, this assumption could change improving the environmental behaviour of this unit.

Flue gas from Titan arrives to the absorption and desorption unit quite clean (for example it is practically free from ash and heavy metals). However, it could contain some impurities such as acid or basic gases (NO<sub>x</sub>, H<sub>2</sub>S, SO<sub>2</sub>, HCl, etc.) in the order of magnitude of ppm. Partners that deal with ionic liquids would like to minimize these pollutants; hence active carbons could be considered for this purpose. In the final LCA model this kind of updates will be included if the partners agree.

Nowadays, specific LCA studies about ionic liquid are scarce [5]. Alviz and Alvarez, (2017) evaluated the potential environmental impacts coming from the use of the ionic liquid 1-butyl-3-methylimidazolium bromide ([Bmim]Br). On this base, the authors of this research work modelled the ionic liquid in terms on LCA. The other items of the inventory were taken from the Ecoinvent 3 database.

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## 2.2.2 Calcium carbonate production.

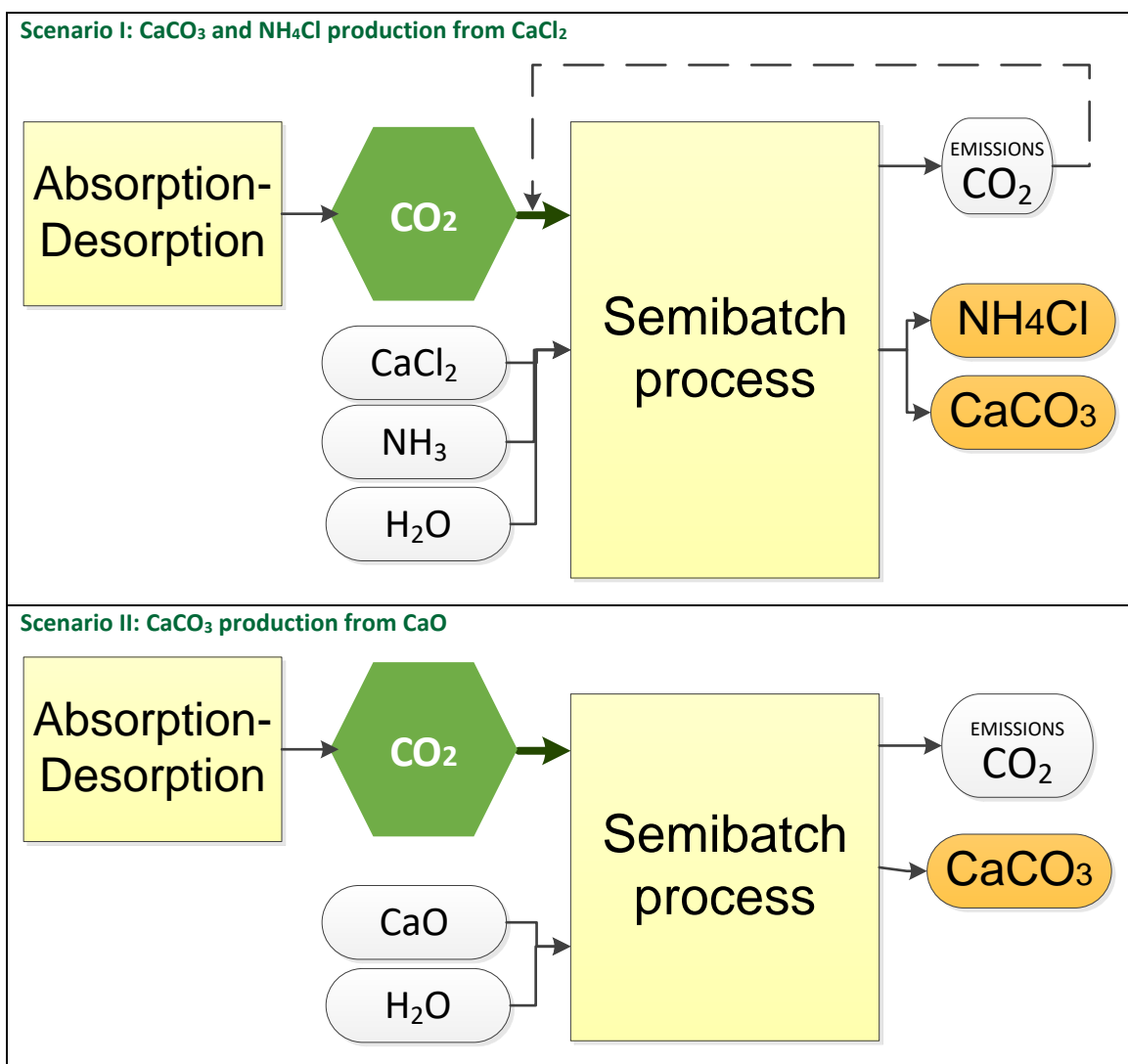



Figure 4. Flowchart of the considered scenarios for  $\text{CaCO}_3$  production. Scenario I represents the simultaneous production of  $\text{CaCO}_3$  and  $\text{NH}_4\text{Cl}$  from  $\text{CaCl}_2$  whereas Scenario II, the single production of  $\text{CaCO}_3$  from  $\text{CaO}$

$\text{CaCO}_3$  was produced by means of different strategies. Figure 4 shows the flowchart of them. Depending on the Ca sources, POLITO partner will get the optimised route for nano $\text{CaCO}_3$  synthesis. These processes will be compared in terms on LCA in order to know the most feasible route from an environmental point of view. Table 2 and Table 3 show the LCI of these different routes. Scenario IA (Table 2) describes the simultaneous production of  $\text{CaCO}_3$  and  $\text{NH}_4\text{Cl}$  from  $\text{CaCl}_2$ . Currently,  $\text{CaCl}_2$  is taken from the ecoinvent database as a calcium chloride from allyl chloride production. However, in next developments this source of calcium could be a waste recovery from other processes like, for example, the Solvay process.

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In Table 2 it is possible to find how the mass flow of CO<sub>2</sub> and energy consumption change by the fact of introducing the unreacted CO<sub>2</sub> in a recovery loop (Scenario I.B). Table 3 provides the LCA inventory data on CaCO<sub>3</sub> production using CaO as source of Ca. Currently, this calcium source is considered as milled quicklime but in future developments could be consider as a recovery from another process such as slag from steel production.

*Table 2. Life Cycle Inventory of simultaneous production of CaCO<sub>3</sub> and NH<sub>4</sub>Cl. Two scenarios Scenario I.A represents a linear process whereas Scenario IB includes CO<sub>2</sub> recovery.*

<b>Outputs</b>	<b>Scenario IA</b>	<b>Scenario IB</b>	
Calcium carbonate	3	3	kg
Ammonium chloride	3.67	3.67	kg
<b>Inputs</b>			
Calcium chloride	4.4	4.4	kg
Ammonia	0.84	0.84	kg
CO <sub>2</sub> 97% from absorption and purification Unit	7.36	1.622	kg
Water, deionised	44.06	44.01	kg
Electricity	15.51	15.71	kWh
<b>Emissions</b>			
Carbon dioxide	<b>6.15</b>	<b>0.9</b>	kg
Water	6.76	6.71	kg
<b>Waste water</b>	37.3	37.3	kg

The RECODE production will be about 3 kg/h of CaCO<sub>3</sub> particles and 3.7 kg/h of NH<sub>4</sub>Cl. To this end, the amounts of calcium chloride and ammonia needed are expressed in Table 2. Regarding the water consumption, Scenario I consumes around 44 kg/h summarized as follows: process consumption around 7 kg/h, 22 kg/h due to the ion exchange and 15 kg/h for the washing process. Washing water and ion exchange water flow in and out as wastewater. Furthermore, process water is evaporated in the oven when particles are dried. Since it was considered that an impurity of the CO<sub>2</sub> inlet stream, supposed to be in the form of water and likely quantified as 3 wt%, there is a slightly different mass flow of H<sub>2</sub>O in the Scenario IA and IB. Regarding electricity consumption, Scenario IA is composed by several pumps (batch, resin columns washing, recycle and resin columns feeding), the oven consumption and the stirring (reservoir tank, stabilization tank and the NH<sub>4</sub>Cl crystallization). Energy consumption in Scenario IB is the same as in Scenario IA but includes an extra compressor for the loop, which recovers the CO<sub>2</sub>.


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Table 3. LCI of the single production of calcium carbonate from CaO.

Products	Scenario II	
Calcium carbonate	3	kg
Inputs		
CaO	1.97	kg
CO <sub>2</sub> 97% from absorption and purification Unit	3.98	kg
Water, deionised	7.5+7.5+(0.064/2)	kg
Electricity	11.6	kWh
Emissions to air		
Oxygen	0.19	kg
Water	7.51	kg
Waste water	7.5	kg
Emissions		
CO <sub>2</sub>	2.66	kg
H <sub>2</sub> O	7.53	kg

The production of CaCO<sub>3</sub> could be carried out by several methods. Recode tends to evaluate some of them in order to decide which one is more technically and environmentally feasible. Table 3 provides the LCA inventory of the 3 kg/h CaCO<sub>3</sub> production from a different source of calcium (CaO). It is apparent, from Table 3, that just one product (CaCO<sub>3</sub>) is produced with the Scenario II whereas with the Scenario I two products are simultaneously produced. Water consumption is 7.5 kg to produce the nanoparticles of CaCO<sub>3</sub>; when CaCO<sub>3</sub> is dried in the oven, this water will be emitted as steam. Furthermore, washing the particles consumes 7.5 kg, which will later be wastewater.

### 2.2.3 Compression and dissolution unit.

Table 4. LCI of the Compression and dissolution unit.

Outputs		
[KIT] CO <sub>2</sub> in ACN/TBAP	0.0176	kg
Inputs		
CO <sub>2</sub> from Absorption/desorption unit	0.01276	kg
TPBAP	1.795028	kg
Acetonitrile	0.079152	kg
Energy	1770	J


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Table 4 shows the LCI of the compression and dissolution unit. This inventory is based on the mass and energy balances provided by KIT. The Inventory presented in the Table 4 represents the materials compressed in one cycle of 30 s. In every 30 s run, the work consumption of the compression process and its simultaneous dissolution is 1770 Joule. With respect to the conventional process (isentropic), the possible energy saving is up to 46% which will be positively reflected in the environmental impacts. Often, the information necessary for the Life Cycle Inventory (LCI) is challenging. Due to the confidentiality of some information concerning production and manufacturing processes, published studies are scarce. TPAP is not included in the common LCA databases. Hence, the proposed correspondence in terms on environmental impacts for this item was Tert-butyl amine.

#### 2.2.4 Electrochemical reactors.

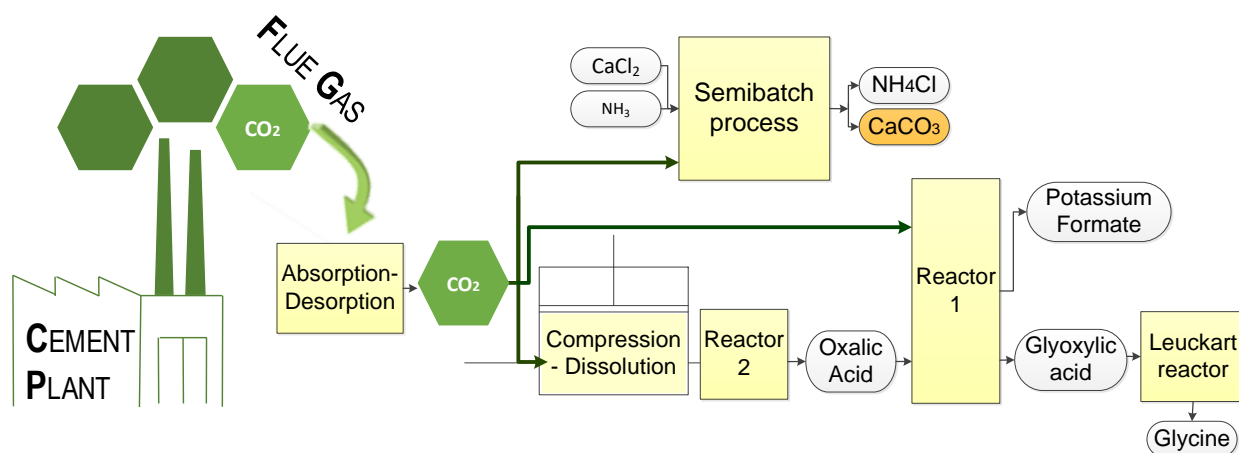



Figure 5. Interim flowchart of RECODE. Provisional layout of the configuration for the electrochemical reactors.

Figure 5 represents a provisional scheme of the configuration for the electrochemical reactors. This configuration is provisional since there is still being developed and discussed by the partners.

##### 2.2.4.1 Zinc Oxalate.

Table 5. LCI of Zinc Oxalate production.

Outputs		
Zinc oxalate	28	kg
Inputs		
Zinc	11.8	kg
CO <sub>2</sub>	22.7	kg
Tetrabutylammonium perchlorate	10.3	kg
Acetonitrile	60	L

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Energy	6120 W·32h/week	
CO <sub>2</sub>	16	kg

Table 5 shows the LCI of the electrocatalytic conversion of CO<sub>2</sub> to oxalate in acetonitrile. AVT partner estimated the amount of chemicals per week. (8h-run, 4 runs). A solution of tetrabutylammonium perchlorate in acetonitrile is used as electrolyte. It can be reused for several runs. For the LCA purpose, it was considered 4 runs. Energy consumption was calculated assuming a cell voltage of 8V and a total current of 765 A with an electrode area = 1.9 m<sup>2</sup>, (45 mA/cm<sup>2</sup>). Apart from the amounts of energy and materials considered, there is CO<sub>2</sub> that does not react. This CO<sub>2</sub> amount could be recirculated and reused. Additional separation steps that are including so far would be needed to connect all the units:


- Acidification of Zinc oxalate to oxalic acid.
- Separation of oxalic acid: liquid-liquid extraction + solvent evaporation.
- Zinc recovery by electrolysis.

### 2.2.5 Potassium formate.

*Table 6. LCI of potassium formate.*

Outputs		
Potassium formate	140	kg
Inputs		
KOH	98	kg
CO <sub>2</sub>	148	kg
H <sub>2</sub> SO <sub>4</sub>	1.5	kg
H <sub>2</sub> O	148	kg
Electricity	5400W·1000h	Wh
Emissions		
H <sub>2</sub>	1	kg
O <sub>2</sub>	27	kg
CO <sub>2</sub> *	70	kg

Table 6 shows the LCI of the electrocatalytic conversion of CO<sub>2</sub> to formate in water. The amount of chemicals was provided per week, 100h-run, 1 run. Energy consumption was calculated assuming a cell voltage of 6V and a total current of 900 A (electrode area = 0.6 m<sup>2</sup>, 150 mA/cm<sup>2</sup>). Regarding the emissions, CO<sub>2</sub> that does not react and could be reused again, so it was not considered for calculations. Additional

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steps that should be developed within RECODE and that would be needed to connect all the units are the separation of potassium formate from potassium bicarbonate and the conversion of potassium formate to ammonium formate to be used for the glycine production. In next updates these developments could be implemented in the LCA model.

#### 2.2.5.1 Glyoxylic acid.


*Table 7. LCI of glyoxylic acid process.*

Outputs		
Glyoxylic acid	19.2	kg
Inputs		
Oxalic acid	31.3	kg
H <sub>2</sub> O	223.7	kg
H <sub>2</sub> SO <sub>4</sub>	9.8	kg
Electricity	1200W·96h	Wh

Electrocatalytic conversion of oxalic acid to glyoxylic acid LCI is reported in Table 7. The energy was taken into account assuming a cell voltage of 6V and a total current of 200 A (electrode area = 0.2 m<sup>2</sup>, 100 mA/cm<sup>2</sup>). Apart from the glyoxylic acid, there are other outputs that were not considered for the analysis: the oxalic acid that is not converted to glyoxylic acid and remains in the electrolyte solution, the emissions of a little amount of hydrogen and oxygen and sulphuric acid and water because they can be reused for other runs. AVT partner reported that, depending on the requirements for the glycine production, possible separation of glyoxylic acid from water could be developed.

#### 2.2.6 Glycine.

Glycine production process is still being developed. Glycine will be synthesised according to a route whose early simulations lead to promising environmental figures. This approach requires specific developments concerning the electrocatalysts and the optimisation of the reductive amination operating conditions to achieve the challenging RECODE targets. The reward will be a good process with an acceptable use of energy and materials resources. As soon as the partner will complete the glycine production development and will report the LCI, the environmental footprint of this approach will be calculated.

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## 2.3 Life Cycle Impact Assessment (LCIA)

The life cycle impact assessment phase (LCIA) is the third phase of the LCA. In LCIA, the inventory is analysed for environmental impact. In this phase of the LCA process, determined impact categories, category indicators and characterization models should be selected. This selection shall be consistent with the goal of the study. The environmental impacts selected for the RECODE LCA will be those from the CML method. CML-IA is a LCA methodology developed by the Center of Environmental Science (CML) of Leiden University in The Netherlands [6]. The CML-IA (baseline) method elaborates the problem-oriented (midpoint) approach. The following CML impacts categories were considered for conducting the RECODE LCA study.

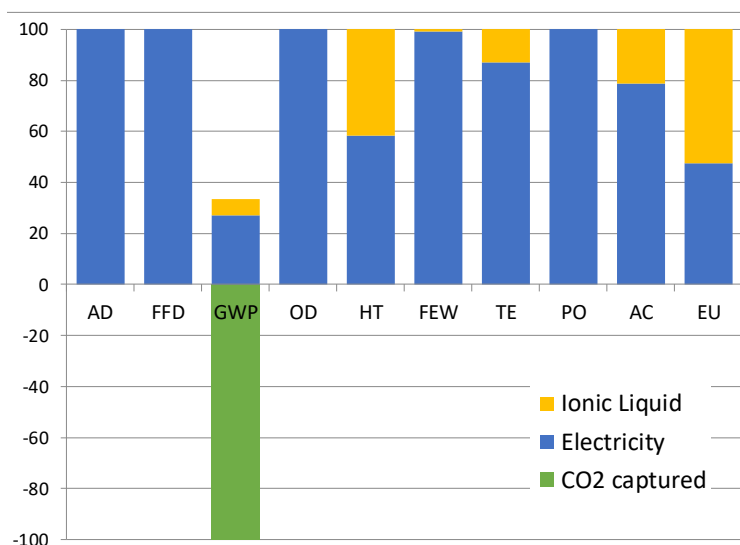
**Abiotic depletion (AD)** category is related to extraction of minerals due to inputs in the system. This category is measured by kg of antimony equivalents. **Depletion of fossil fuels (FFD)** is expressed in MJ per kg of m<sup>3</sup> fossil fuel, fossil fuels being considered to be fully substitutable. **Global warming potential (GWP)** was developed by the Intergovernmental Panel on Climate Change. Global Warming Potential for time horizon 100 years (GWP100) is expressed in kg of carbon dioxide equivalent. **Ozone layer depletion (OD)** is developed by the World Meteorological Organisation and defines ozone depletion potential of different gases (kg of CFC-11 equivalent). **Human toxicity (HT)**, **Freshwater aquatic ecotoxicity (FEW)**, and **Terrestrial ecotoxicity (TE)** describe fate, exposure and effects of toxic substances for an infinite time horizon expressed as 1,4-dichlorobenzene equivalents. The model for **photochemical oxidation (PO)** was developed by Jenkin & Hayman and Derwent [7] and defines photochemical oxidation expressed in kg of ethylene. **Acidification (AC)** potential is expressed in kg of SO<sub>2</sub> equivalents, the model was developed by Huijbregts [8]. **Eutrophication (EU)** potential is expressed in kg of PO<sub>4</sub> equivalents per kg of emission.

Finally, life cycle interpretation is the final phase of the LCA procedure, in which the results of an LCI or an LCIA, or both, are summarized and discussed as a basis for conclusions, recommendations and decision-making in accordance with the goal and scope definition. This step will be assessed in the next sections. Emphasis will be placed on evaluating the CO<sub>2</sub> that impact on the Global Warming Potential.



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### 2.3.1 Absorption and desorption unit.



**Figure 6. Environmental impacts of 1 kg of CO<sub>2</sub> purified. Contributions in %.**

**Table 8. Environmental impacts of 1 kg of CO<sub>2</sub> purified.**

Impact category	Unit	Total
<b>AD</b>	kg Sb eq	2.9E-07
<b>FFD</b>	MJ	3.3E+00
<b>GWP</b>	kg CO <sub>2</sub> eq	-6.6E-01
<b>OD</b>	kg CFC-11 eq	2.8E-08
<b>HT</b>	kg 1,4-DB eq	6.3E-02
<b>FEW</b>	kg 1,4-DB eq	6.7E-03
<b>TE</b>	kg 1,4-DB eq	2.5E-03
<b>PO</b>	kg C <sub>2</sub> H <sub>4</sub> eq	5.2E-05
<b>AC</b>	kg SO <sub>2</sub> eq	1.6E-03
<b>EU</b>	kg PO <sub>4</sub> <sup>---</sup> eq	3.1E-04

Table 8 shows the results of 1 kg of CO<sub>2</sub> purified in the absorption and desorption unit. Ten environmental categories were assessed and reported. Figure 6 shows the impact contribution of the items involved in the process. CO<sub>2</sub> from the cement plant flue gas is absorbed by means of ionic liquid with energy consumption. AD, FFD, OD, FEW and PO are the impacts most influenced by the electricity consumption. Instead, HT, TE, AC and EU present a noticeable contribution by the ionic liquid. There is a significant outcome regarding the GWP. This impact category is measured in kg CO<sub>2</sub> equivalents. This fact makes the CO<sub>2</sub> capture presenting a negative contribution. This negative value has a positive connotation. The potential CO<sub>2</sub> produced by this unit is lower than what is able to capture from the flue gas. Per every single kg of CO<sub>2</sub> purified, the CO<sub>2</sub> potentially saved is 0.66 kg equivalent. The other 0.34 kg of CO<sub>2</sub> are shared between the electricity consumption, which represents 0.27 kg CO<sub>2</sub> eq, and the use of ionic liquid with 0.07 kg CO<sub>2</sub> eq. This is the only unit in which CO<sub>2</sub> emissions are negative, provoking a positive result in terms on GWP. This result will be considered upstream of other processes. Thus, the improvement of this unit will improve the overall plant.

## 2.3.2 Calcium carbonate production.

### 2.3.2.1 Comparative

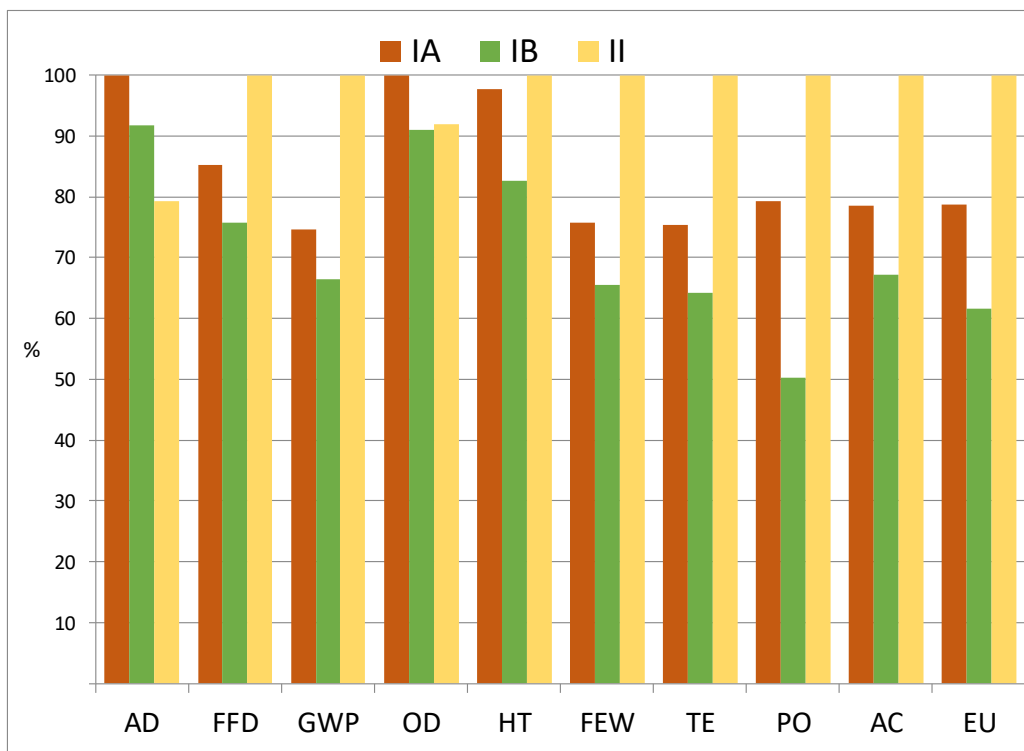



Figure 7 Comparative LCA of three scenarios of CaCO<sub>3</sub> production.

Table 9. Environmental impacts of 1 kg of CaCO<sub>3</sub> in every scenario.

Impact category	Unit	IA	IB	II
AD	kg Sb <sub>eq</sub>	3.70E-06	3.40E-06	2.93E-06
FFD	MJ	3.03E+01	2.69E+01	3.55E+01
GWP	kg CO <sub>2</sub> eq	2.14E+00	1.90E+00	2.86E+00
OD	kg CFC-11 <sub>eq</sub>	3.04E-07	2.76E-07	2.79E-07
HT	kg 1,4-DB <sub>eq</sub>	3.89E-01	3.30E-01	3.98E-01
FEW	kg 1,4-DB <sub>eq</sub>	4.71E-02	4.09E-02	6.23E-02
TE	kg 1,4-DB <sub>eq</sub>	1.54E-02	1.31E-02	2.05E-02
PO	kg C <sub>2</sub> H <sub>4</sub> eq	7.07E-04	4.49E-04	8.93E-04
AC	kg SO <sub>2</sub> eq	1.02E-02	8.77E-03	1.30E-02
EU	kg PO <sub>4</sub> <sup>---</sup> eq	1.34E-03	1.05E-03	1.70E-03

The LCA results of the three assessed scenarios are shown in Table 9, which presents the environmental impact results in ten CML categories of 1 kg of CaCO<sub>3</sub>.

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In the observation of the single impact categories, it is possible to specify that environmental impacts of scenario IA are higher than those of scenario IB in all the assessed categories. This means that the fact of recirculate some part of CO<sub>2</sub> leads to improve the initially thought approach (scenario IA). In general, Scenario I (A and B) gets lower potential environmental impacts than Scenario II, except for the AD indicator in which the production of calcium carbonate from calcium chloride obtains higher impact than the production of calcium carbonate from calcium oxide. In terms of LCA, the overview of the results suggests that the most promising technology for the CaCO<sub>3</sub> production among the three analyzed routes is the Scenario IB where nanoparticles are simultaneously with NH<sub>4</sub>Cl and produced from CaCl<sub>2</sub> as the calcium source.

In order to know the main contributing phases for each impact category, a contribution analysis was included. This will be assessed in the following sections.

### 2.3.2.2 Scenario I

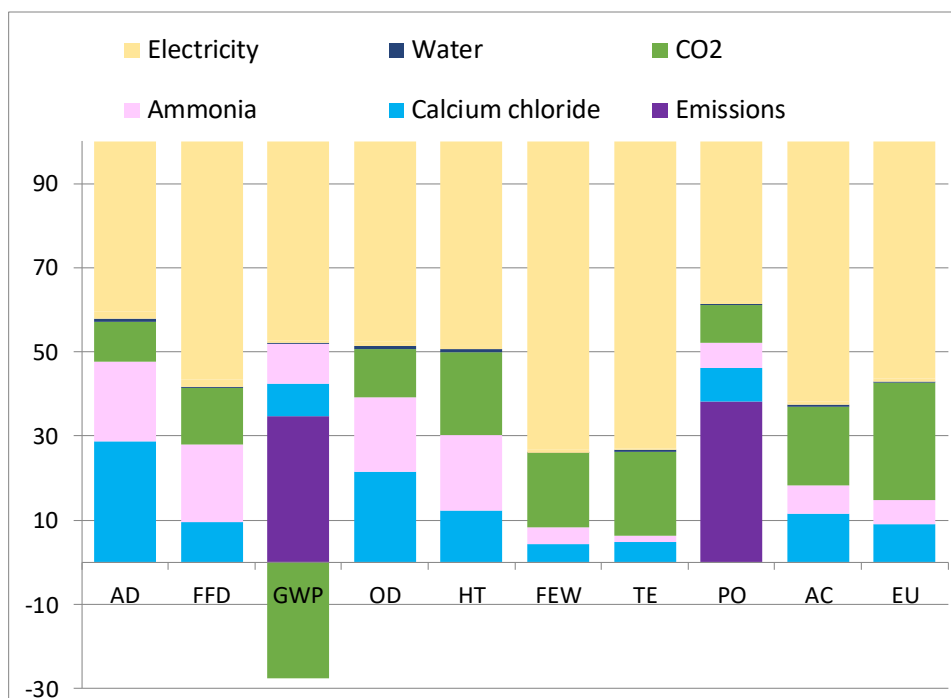



Figure 8. Environmental impacts of 1 kg of CaCO<sub>3</sub> in Scenario IA. Contributions in %.

GWP of scenario IA is 2.14 kg of CO<sub>2</sub> eq/ kg of CaCO<sub>3</sub> produced. This amount is influenced by the elements of the system. Environmental impacts breakdown of GWP resulted in 1.02 kg of CO<sub>2</sub> eq due to the emissions, 0.23 kg of CO<sub>2</sub> eq due to the calcium chloride and 0.28 kg of CO<sub>2</sub> eq due to the ammonia. The

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most interesting aspect of this graph lies in the contribution of the upstream captured CO<sub>2</sub> in the absorption and desorption plant. This fact is represented by -0.81 kg of CO<sub>2</sub> eq. Water consumption use barely represents 1% of the GWP. However, the impact contribution with highest CO<sub>2</sub> eq is the electricity (1.4 kg of CO<sub>2</sub> eq).

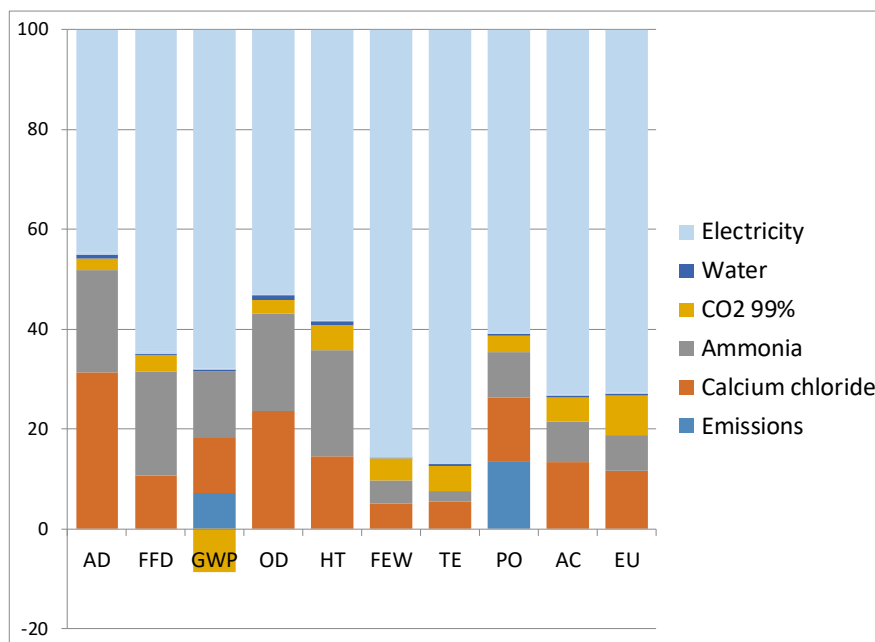
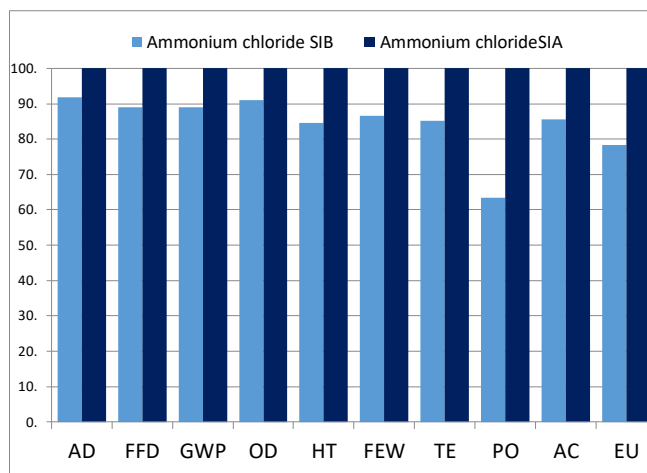


Figure 9. Environmental impacts of 1 kg of CaCO<sub>3</sub> in Scenario IB. Contributions in %.

Figure 9 represents the results obtained for 1 kg of CaCO<sub>3</sub> produced in the scenario IB, which simultaneously produce CaCO<sub>3</sub> and NH<sub>4</sub>Cl. The main difference with Scenario IA is a CO<sub>2</sub> recovery loop in the Scenario IB. For producing 3 kg CaCO<sub>3</sub>/h, Scenario IA presents an input of 7.36 kg of CO<sub>2</sub> but an output of 6.15 kg of CO<sub>2</sub> as emissions. If a considerable amount of CO<sub>2</sub> is recirculated (Scenario IB) the in/out flow rates decrease (as declare in the LCI, Table 2). The addition of this loop involves a certain amount of energy consumption associated to the compressor. However, looking at the GWP (Table 9 or Figure 7), it is possible to notice that the GWP in Scenario IB is 1.9 kg CO<sub>2</sub>eq/kg CaCO<sub>3</sub> whereas in the scenario IA is 2.14 kg CO<sub>2</sub>eq/kg CaCO<sub>3</sub>. Concerning Figure 9, it is also interesting that the energy demand is responsible for the highest contribution to the impacts in all the assessed categories, followed by calcium chloride and ammonia.




*Figure 10 Comparative LCA of two possibilities of ammonium chloride production.*

*Table 10. Environmental Impacts of 1 kg of ammonium chloride in the two possible scenarios.*

Impact category	Unit	Ammonium chloride SIA	Ammonium chloride SIB
AD	kg Sb eq	3.02E-06	2.78E-06
FFD	MJ	2.48E+01	2.20E+01
GWP	kg CO <sub>2</sub> eq	1.75E+00	1.56E+00
OD	kg CFC-11 eq	2.48E-07	2.26E-07
HT	kg 1,4-DB eq	3.18E-01	2.69E-01
FEW	kg 1,4-DB eq	3.85E-02	3.34E-02
TE	kg 1,4-DB eq	1.26E-02	1.07E-02
PO	kg C <sub>2</sub> H <sub>4</sub> eq	5.78E-04	3.67E-04
AC	kg SO <sub>2</sub> eq	8.37E-03	7.17E-03
EU	kg PO <sub>4</sub> --- eq	1.10E-03	8.59E-04

Figure 10 and Table 10 represent the environmental impacts of 1 kg of NH<sub>4</sub>Cl produced in the two assessed scenarios for RECODE. GWP in Scenario IA was 1.75 kg CO<sub>2</sub> eq/kg NH<sub>4</sub>Cl, in scenario IB 1.56 kg CO<sub>2</sub> eq/kg NH<sub>4</sub>Cl. It is possible to notice as the scenario IB gets environmental benefits in all the categories assessed. The fact of recirculate CO<sub>2</sub> not only improve the environmental behavior of the CaCO<sub>3</sub> but also the NH<sub>4</sub>Cl production.

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### 2.3.2.3 Scenario II

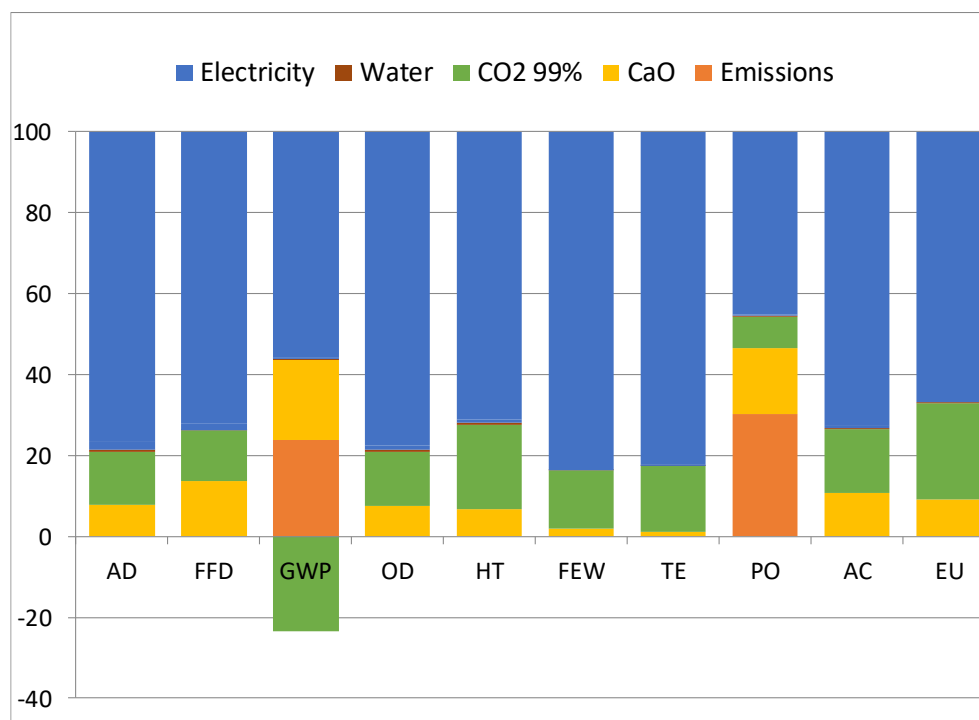



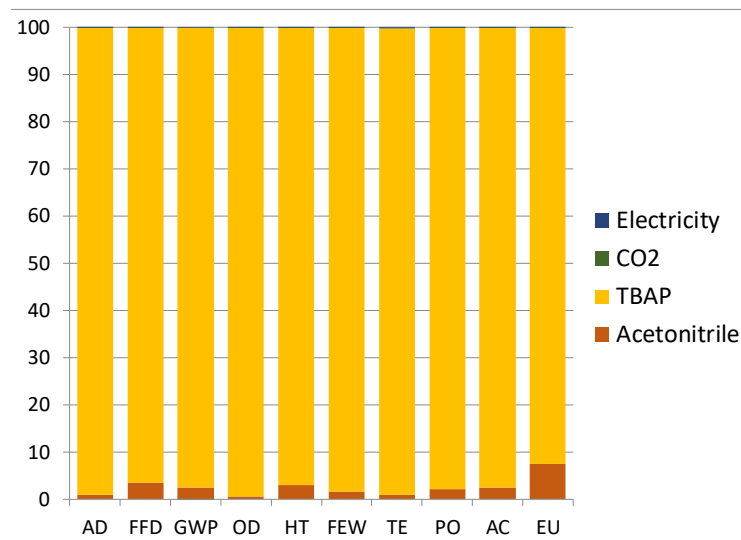
Figure 11. Environmental impacts of 1 kg of  $\text{CaCO}_3$  in Scenario II. Contributions in %.

Figure 11 represents the breakdown of impact contribution in the scenario II. Here it is possible to notice, again, how the main contributor to the impacts is the electricity. Nevertheless, CaO has lower environmental impacts than their analogous source of calcium in Scenario I ( $\text{CaCl}_2$ ). Turning back into Figure 7, AD presented higher results in Scenario I (A and B) than in Scenario II. In scenario I is it possible to notice that calcium chloride consumption represents a considerable amount of percentage contribution in the depletion of abiotic resources (AD). However, in Scenario II the source of calcium (CaO) has lower contribution in this category. This fact makes the AD category the only one in which scenario II gets better results than Scenario I.

Regarding the processes upstream, the negative contribution of the  $\text{CO}_2$  captured in the absorption and purification unit is represented and contributes favorably to the GWP. Water consumption is a contribution almost negligible. Emissions represents more than 20% in GWP and OP categories.

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### 2.3.3 Compression and dissolution unit.




**Figure 12** Environmental impacts of 1 kg of CO<sub>2</sub> compressed and dissolved in CAN/TBAP. Contributions in %.

**Table 11.** Environmental impacts of 1 kg of CO<sub>2</sub> compressed and dissolved in CAN/TBAP

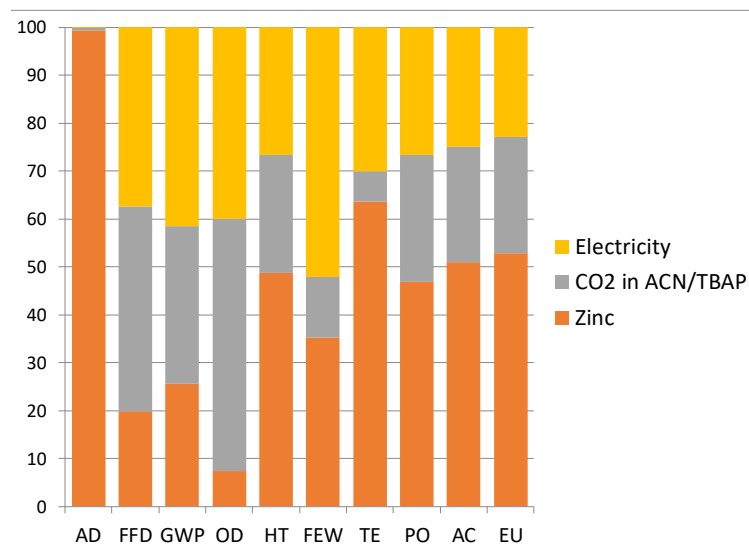
Impact category	Unit	Total
<b>AD</b>	kg Sb <sub>eq</sub>	4.68E-05
<b>FFD</b>	MJ	1.33E+02
<b>GWP</b>	kg CO <sub>2</sub> eq	7.51E+00
<b>OD</b>	kg CFC-11 <sub>eq</sub>	1.30E-06
<b>HT</b>	kg 1,4-DB <sub>eq</sub>	1.18E+00
<b>FEW</b>	kg 1,4-DB <sub>eq</sub>	5.78E-02
<b>TE</b>	kg 1,4-DB <sub>eq</sub>	1.59E-02
<b>PO</b>	kg C <sub>2</sub> H <sub>4</sub> eq	1.82E-03
<b>AC</b>	kg SO <sub>2</sub> eq	4.15E-02
<b>EU</b>	kg PO <sub>4</sub> <sup>---</sup> eq	5.45E-03

Table 11 represents the LCA of 1 kg of CO<sub>2</sub> compressed in the piston of the compression and dissolution unit. Figure 12 shows the environmental contributions in %. Here it is possible to notice the contributions to the impacts of the products used in the compression. Usually, in this kind of processes, energy consumption gets a high contribution into the impacts, but KIT is saving more than 40% with respect to a conventional process and this is reflected positively in the results. It is possible to appreciate that the electricity has a negligible contribution. However, TBAP presents the most striking environmental hazards of this system. Hence, efforts should be oriented in replace this material if the environmental footprint is wanted to be reduced.

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## 2.3.4 Electrochemical reactors.

### 2.3.4.1 Zinc Oxalate.




**Figure 13 Environmental impacts of 1 kg of Zinc Oxalate. Contributions in %.**

**Table 12 Environmental impacts of 1 kg of Zinc Oxalate.**

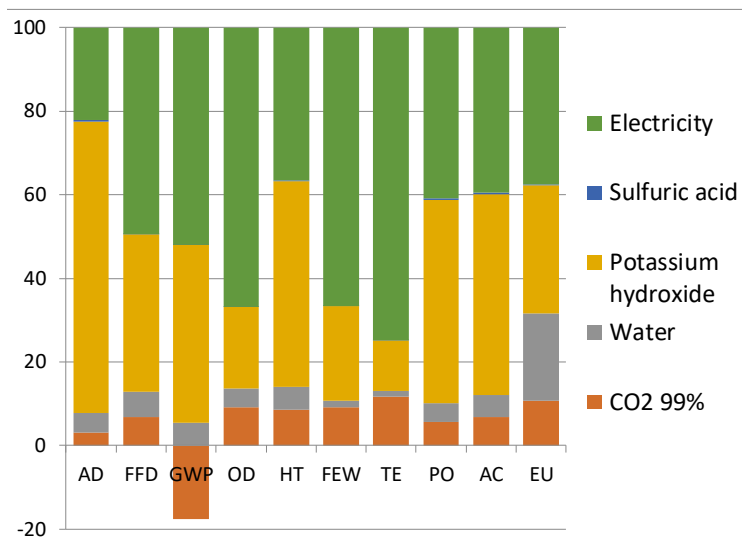
Impact category	Unit	Total
<b>AD</b>	kg Sb <sub>eq</sub>	4.11E-03
<b>FFD</b>	MJ	1.24E+02
<b>GWP</b>	kg CO <sub>2</sub> eq	9.10E+00
<b>OD</b>	kg CFC-11 <sub>eq</sub>	9.80E-07
<b>HT</b>	kg 1,4-DB <sub>eq</sub>	1.92E+00
<b>FEW</b>	kg 1,4-DB <sub>eq</sub>	1.80E-01
<b>TE</b>	kg 1,4-DB <sub>eq</sub>	1.01E-01
<b>PO</b>	kg C <sub>2</sub> H <sub>4</sub> eq	2.74E-03
<b>AC</b>	kg SO <sub>2</sub> eq	6.86E-02
<b>EU</b>	kg PO <sub>4</sub> <sup>---</sup> eq	8.93E-03

Table 12 provides the results obtained from the preliminary LCA of 1 kg of Zinc oxalate produced in the RECODE project. Results revealed that the AD category was dominated by the zinc used. Regarding Figure 13, for the other nine impact categories assessed, electricity and the CO<sub>2</sub> compressed and dissolved in CAN/TBAP produce a considerable amount of impacts. In the GWP case, more than 20% of the impact is due to the Zn use and more than 30% due to the CO<sub>2</sub> compressed that carries its own upstream environmental burden. The electricity provokes a contribution of more than 30% in the GWP.



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### 2.3.4.2 Potassium formate.




**Figure 14 Environmental impacts of 1 kg of potassium formate. Contributions in %.**

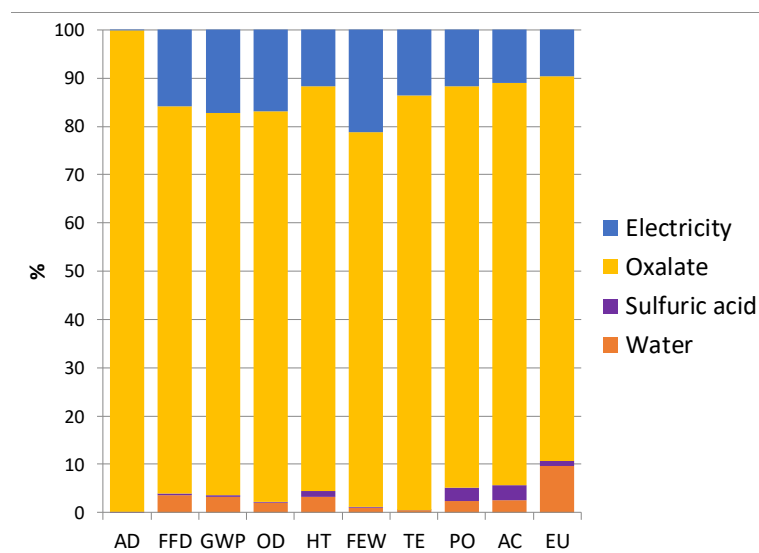
**Table 13 Environmental impacts of 1 kg of potassium formate.**

Impact category	Unit	Total
<b>AD</b>	kg Sb <sub>eq</sub>	1.0E-05
<b>FFD</b>	MJ	5.2E+01
<b>GWP</b>	kg CO <sub>2</sub> eq	3.3E+00
<b>OD</b>	kg CFC-11 <sub>eq</sub>	3.2E-07
<b>HT</b>	kg 1,4-DB <sub>eq</sub>	7.7E-01
<b>FEW</b>	kg 1,4-DB <sub>eq</sub>	7.7E-02
<b>TE</b>	kg 1,4-DB <sub>eq</sub>	2.2E-02
<b>PO</b>	kg C <sub>2</sub> H <sub>4</sub> eq	9.8E-04
<b>AC</b>	kg SO <sub>2</sub> eq	2.4E-02
<b>EU</b>	kg PO <sub>4</sub> <sup>---</sup> eq	3.0E-03

Table 13 presents the results in terms on LCA of 1 kg of potassium formate in ten categories of the CML method. Figure 14 shows how the different items considered in this study affect the environmental impacts in %. In this regard, potassium hydroxide and electricity have the major contributions in all categories. Likewise, water consumption remains under 10% of the impacts unless in the eutrophication category (EU). The production of potassium formate takes CO<sub>2</sub> directly from the absorption-desorption unit. With this in mind, it is possible (negative value) to notice the positive contribution in the GWP category. However, in the other nine categories, this CO<sub>2</sub> consumption produce environmental impacts. The contribution to CO<sub>2</sub> from the absorption and desorption unit to the impact categories is under 10% except in the TE and EU impacts in which reaches 11.8% and 10.8% respectively.

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### 2.3.4.3 Glyoxylic acid.




**Figure 15 Environmental impacts of 1 kg of glyoxylic acid. Contributions in %.**

**Table 14. Environmental impacts of 1 kg of glyoxylic acid**

Impact category	Unit	Total
<b>AD</b>	kg Sb <sub>eq</sub>	6.72E-03
<b>FFD</b>	MJ	2.52E+02
<b>GWP</b>	kg CO <sub>2</sub> eq	1.88E+01
<b>OD</b>	kg CFC-11 <sub>eq</sub>	1.98E-06
<b>HT</b>	kg 1,4-DB <sub>eq</sub>	3.74E+00
<b>FEW</b>	kg 1,4-DB <sub>eq</sub>	3.78E-01
<b>TE</b>	kg 1,4-DB <sub>eq</sub>	1.92E-01
<b>PO</b>	kg C <sub>2</sub> H <sub>4</sub> eq	5.37E-03
<b>AC</b>	kg SO <sub>2</sub> eq	1.34E-01
<b>EU</b>	kg PO <sub>4</sub> <sup>---</sup> eq	1.83E-02

The production of 1 kg of glyoxylic acid by means of the RECODE processes has an environmental footprint depicted in Table 14 and Figure 15. Table 14 expresses the numerical values of the 10 categories assessed by CML method whereas Figure 15 explain how these categories are affected by their components. What Figure 15 highlights is that glyoxylic acid environmental impacts are dominated by the oxalate used in the process. Water and sulphuric acid do not present high values in the impacts. The energy consumption represents from almost 10 to 20% in all impacts except for AD, in which is negligible.

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### 3 REACH analysis

REACH is a regulation of the European Union, adopted to improve the protection of human health and the environment from the risks that can be posed by chemicals, while enhancing the innovation and competitiveness of the EU chemicals industry. This is done by the four processes of REACH, namely the registration, evaluation, authorisation and restriction of chemicals [9]. It also promotes alternative methods for the hazard assessment of substances in order to reduce the number of tests on animals. It entered into force on 1 June 2007 [9].

One of the main reasons for developing and adopting the REACH Regulation was that a large number of substances have been manufactured and placed on the market in Europe for many years, sometimes in very high amounts, and yet there is insufficient information on the hazards that they pose to human health and the environment. There is a need to fill these information gaps to ensure that industry is able to assess hazards and risks of the substances, and to identify and implement the risk management measures to protect humans and the environment [10].

In principle, REACH applies to all chemical substances; not only those used in industrial processes but also in our day-to-day lives, for example in cleaning products, paints as well as in articles such as clothes, furniture and electrical appliances. Therefore, the regulation has an impact on most companies across the EU [11].

Within the RECODE project, the REACH study was implemented, first in order to activate a procedure for collecting and assessing information on the properties and hazards of substances involved in the project; second, to check those chemicals against the REACH directives in order to avoid impact on workers' health and release of harmful chemicals into the environment. Finally, it was carried out to provide appropriate safety information for the consortium, especially, to the users.

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### 3.1 Chemical Information

Substances and chemicals involved in the overall process (CO<sub>2</sub> purification, nano-CaCO<sub>3</sub> and electrochemical reactors units) have been identified in order to study their intrinsic properties. The following Figure illustrate the procedure followed to perform the analysis.



Figure 16. Steps for the Reach analysis.

Figure 17 shows the overall concept of RECODE divided in the main sub-units of that will be developed. RECODE project will demonstrate the capacity of utilization of CO<sub>2</sub> conversion products within the same cement business. In the RECODE approach, the products of CO<sub>2</sub> conversion are used inside the same plant to produce high-quality cement and at the same time reducing resource and energy intensity. So, flue gas stream, CO<sub>2</sub>, CaCl<sub>2</sub>, NH<sub>3</sub>, nano-CaCO<sub>3</sub>, NH<sub>4</sub>Cl, formic acid, oxalic acid and glycine are at the project battery limit.

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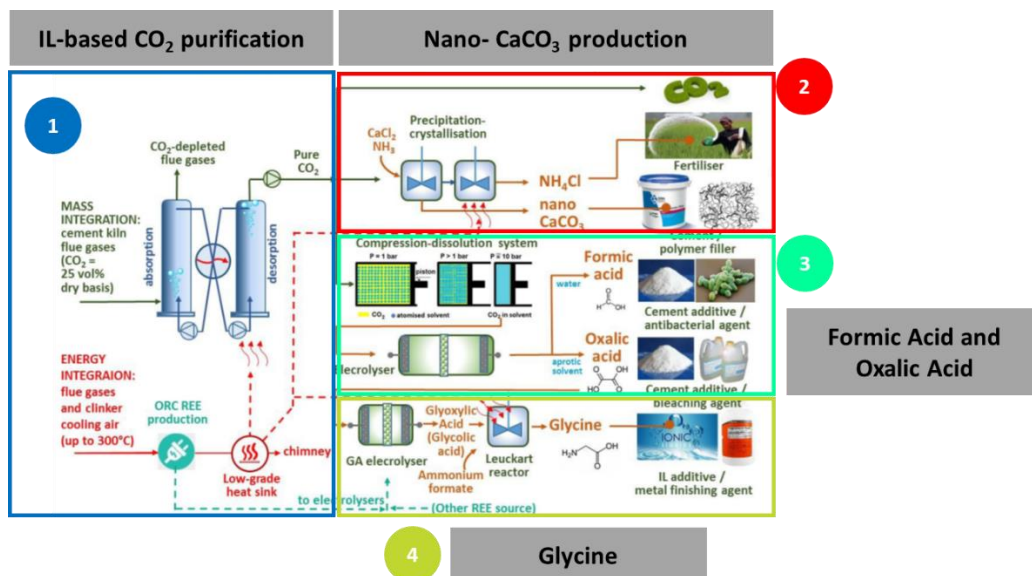



Figure 17. RECODE concept divided in its main sub-units (IL-based CO<sub>2</sub> purification, Nano-CaCO<sub>3</sub> production, formic acid and oxalic acid, glycine units).

### 3.1.1 Unit -01: CO<sub>2</sub> purification

The process involves the capture and purification of the CO<sub>2</sub> from the flue gas stream coming from the Kamari cement plant (TITAN). Properties and hazards of substances used into CO<sub>2</sub> absorption unit.

Table 15. Information of the properties and hazards of substances involved in U-01

Substance	N° CAS	Hazard identification	Exposure time/h	Mass(g) or volume (L) of the product/h	Other information
Functionalised ionic liquid [BDiMIM]Pro	n/a	n/a	Only upon loading/unloading the absorption unit	Ca. 100 L/month	CO <sub>2</sub> absorption Unit (Unit-01). Final selection of ILs still pending!
Solvent ionic liquid [BDiMIM]NTf <sub>2</sub>	350493-08-2	H301, H318	Only upon loading/unloading the absorption unit	Ca. 10 L/month	CO <sub>2</sub> absorption Unit (Unit-01). Final selection of

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					ILs still pending!
Flue gas (feed)	n/a	n/a risk of asphyxiation	No exposure expected	Ca. 50 m <sup>3</sup> /h	CO <sub>2</sub> absorption Unit (Unit-01)
CO <sub>2</sub>	124-38-9	n/a risk of asphyxiation	No exposure expected	Ca. 5 m <sup>3</sup> /h	CO <sub>2</sub> absorption Unit (Unit-01)

Flue gas can be interpreted by process gases. It is covered by Annex V of the REACH and are exempted from the following Parts of REACH: Title II (Registration); Title V (Downstream Users); Title VI (Evaluation). This means that, their registration is deemed inappropriate or unnecessary [12].

- **Carbon dioxide**


CO<sub>2</sub> is covered by Annex IV of the REACH and it is exempted from the Titles II (registration), Title V (downstream user regulation), Title VI (evaluation) and Title VIII (Authorization) of REACH. Substances included in Annex IV, as sufficient information is known about these substances that they are considered to cause minimum risk because of their intrinsic properties.


- EC / List no: 204-696-9
- CAS no: 124-38-9|

**Carbon dioxide**

[Translated names 21](#)
[IUPAC names 2](#)
[Other identifiers 1](#)

**Substance identity**  
EC / List no.: 204-696-9  
CAS no.: 124-38-9  
Mol. formula: CO2

? **Hazard classification & labelling**  
 According to the majority of notifications provided by companies to ECHA in CLP notifications no hazards have been classified.

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- Ionic liquid**

As example, while is selected the final IL for the RECODE project, 1-Butyl-3-methylimidazolium Bis(trifluoromethanesulfonyl)imide has been used for the study.

**1-Butyl-3-methylimidazolium Bis(trifluoromethanesulfonyl)imide**

Regulatory process names 1 IUPAC names 2 Other identifiers 1

**Substance identity**

**EC / List no.:** 605-742-4  
**CAS no.:** 174899-83-3  
**Mol. formula:**  
C1=CC=C(C=C1)[N+]1C=CC=C1C(F)(F)F


**Hazard classification & labelling**



*Danger!* According to the classification provided by companies to ECHA in **CLP notifications** this substance is toxic if swallowed, is toxic in contact with skin, causes severe skin burns and eye damage, is toxic to aquatic life with long lasting effects and may cause damage to organs through prolonged or repeated exposure.

With the following hazard identification

H314	Causes severe skin burns and eye damage.
H373	May cause damage to organs through prolonged or repeated exposure.
H411	Toxic to aquatic life with long lasting effects.
H301+H311	Toxic if swallowed or in contact with skin.

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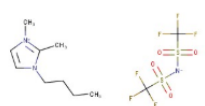
- **Solvent ionic liquid**


**1-Butyl-2,3-dimethylimidazolium Bis(trifluoromethanesulfonyl)imide**

---

IUPAC names 1 Other identifiers 1

---

**Substance identity**  
EC / List no.: 700-236-0  
CAS no.: 350493-08-2  
Mol. formula:  


**Hazard classification & labelling**  
  
Warning! According to the classification provided by companies to ECHA in **CLP notifications** this substance causes serious eye irritation and causes skin irritation.


### 3.1.2 Unit-02: Nano-CaCO<sub>3</sub> production

Nanosized CaCO<sub>3</sub> particles added to cement not only activate the cement hydration, but they enhance the mechanical properties such as flexural and compressive strength. Information about the reagent used for the production of nano particles are reported in Table 16.

Table 16. Information of the properties and hazards of substances used in U-02.

Substance	N° CAS	Hazard identification	Exposure time/h	Mass(g) or volume (L) of the product/h	Other information
Calcium chloride (CaCl <sub>2</sub> )	10043-52-4	H319 - -	Only upon loading/unloading the reactor (10 min/h)	4400 g/h	Nano CaCO <sub>3</sub> Production Unit (Unit-02)
Ammonium hydroxide (NH <sub>4</sub> OH)	1336-21-6	H302 H314 H400	Only upon loading/unloading the reactor (10 min/h)	1740 g/h	Nano CaCO <sub>3</sub> Production Unit (Unit-02)
Carbon dioxide (CO <sub>2</sub> )	124-38-9	H280		8230 g/h	Nano CaCO <sub>3</sub> Production Unit (Unit-02)
Calcium carbonate (CaCO <sub>3</sub> )	471-34-1	H315 H320 H335	Filter unloading (10 min/h)	3000 g/h	Nano CaCO <sub>3</sub> Production



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					Unit (Unit-02)
Ammonium chloride (NH <sub>4</sub> Cl)	12125-02-9	H302	Filter unloading (10 min/h)	3600 g/h	Nano CaCO <sub>3</sub> Production Unit (Unit-02)

### 3.1.3 Unit-03 and Unit-04: Formic, Oxalic and Glyoxylic acid production


All chemicals used to produce formic and oxalic acid are described in the following table.

*Table 17. Information of the properties and hazards of substances used in U-03 and U-04.*

Substance	N° CAS	Hazard identification	Exposure time/h	Mass(g) or volume (L) of the product/h	Other information
CO <sub>2</sub>	124-38-9	H280		23 kg/week Estimation for 8h-run, 4 runs per week	Oxalate production PU-302
Acetonitrile	75-05-8	H225- H302+H312+H332- H319		60 L/week Estimation for 8h-run, 4 runs per week	Oxalate production PU-302
Tetrabutylammonium perchlorate (TBAP)	2567-83-1	H272- H315+H319+H335		11 kg/week Estimation for 8h-run, 4 days per week	Oxalate production PU-302
Zinc oxalate	208-934-2	n.a. Based on sodium oxalate: H302+H312		28 kg/week Estimation for 8h-run, 4 runs per week (reaction product)	Oxalate production PU-302
CO <sub>2</sub>	124-38-9	H280		148 kg/week Estimation for 100h-	Formate production PU-303

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				run, 1 run per week	
Potassium hydroxide	1310-58-3	H290, H302, H314		98 kg/week Estimation for 100h- run, 1 run per week	Formate production PU-303
Sulfuric acid	7664-93-9	H290, H314		1.5 kg/week Estimation for 100h- run, 1 run per week	Formate production PU-303
Potassium formate	590-29-4	-		140 kg/week Estimation for 100h- run, 1 run per week (reaction product)	Formate production PU-303
Potassium bicarbonate	298-14-6	-		7 kg/week Estimation for 100h- run, 1 run per week (reaction product)	Formate production PU-303
Oxalic acid	6153-56-6	H302+H312, H318		32 kg/week Estimation for 24h-run, 4 days per week	Glyoxylic acid/Glycine production PU-401
Sulfuric acid	7664-93-9	H290, H314		10 kg/week Estimation for 24h-run, 4 days per week	Glyoxylic acid/Glycine production PU-401
Glyoxylic acid	563-96-2	H317, H318		19 kg/week Estimation for 24h-run, 4 days per week	Glyoxylic acid/Glycine production PU-401

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				(reaction product)	
Formic acid	64-18-6	H226, H302, H314			Formate production PU-303
Glycine	56-40-6	-			Glyoxylic acid/Glycine production PU-401

### 3.2 Personal protection Equipment

All these substances can be safely used; however, the previous information was collected to communicate the risk management measures to the users. The consortium and personnel that will work in the final demonstration plant need to be aware about the intrinsic properties and hazard of the chemicals and materials that are being used in the overall plant. Furthermore, during the lab scale tests and also during the final demonstration campaign when the chemicals will be handled, the following PPE must be used:



Eye/face protection: Face shield and safety glasses should be use. Use equipment for eye protection tested and approved under appropriate government standards such as NIOSH (US) or EN 166(EU).



Respiratory protection: Use appropriated air-purifying respirators (full-face particle respirator type N100 (US) or type P3 (EN 143) respirator).


Use respirators and components tested and approved under appropriate government standards such as NIOSH (US) or CEN (EU).



Skin protection: when handle the chemicals/substances use proper gloves.

Gloves must be inspected prior to use. Use proper glove removal technique (without touching glove's outer surface) to avoid skin contact with this product. Dispose of contaminated gloves after use in accordance with applicable laws and good laboratory practices.

Wash and dry hands.

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The selected protective gloves must satisfy the specifications of EU Directive 89/686/EEC and the standard EN 374 derived from it.

Body Protection: Complete suit protecting against chemicals, the type of protective equipment must be selected according to the concentration and amount of the dangerous substance at the specific workplace.

### 3.3 Toxicity assessment

For some substances, it was decided to study their particular nature in the context of the REACH analysis. This is the case of  $\text{CaCO}_3$ , whose size distribution is relevant as far as health and safety effects are concerned. After a preliminary assessment of the possible toxic effects of  $\text{CaCO}_3$  NPs by cell viability on two different cell lines (ref. D4.1), it was evaluated their possible induction of intracellular oxidative stress and DNA damage (work done at IIT). First, the ability of  $\text{CaCO}_3$  NPs to produce ROS was measured with the 2'-dichlorodihydrofluorescein diacetate (DCFH-DA) assay. The experimental conditions were similar to the ones of previous toxicity studies. We exposed mouse embryonic fibroblasts (NIH 3T3 cells) and human breast adenocarcinoma cells (MCF7 cells) to different concentrations of  $\text{CaCO}_3$  NPs (1, 5, 10, 25 and  $50 \mu\text{g mL}^{-1}$ ) for 2, 6 and 24 h. In NIH 3T3, the intracellular ROS level was not increased by exposure to any concentrations of  $\text{CaCO}_3$  NPs, in comparison with the unexposed cells (Figure 18A). A similar trend is observable also in the case of MCF7 cells for all the time points and concentration tested (Figure 18B). These results indicate that  $\text{CaCO}_3$  NPs do not induce oxidative stress in both cell lines.

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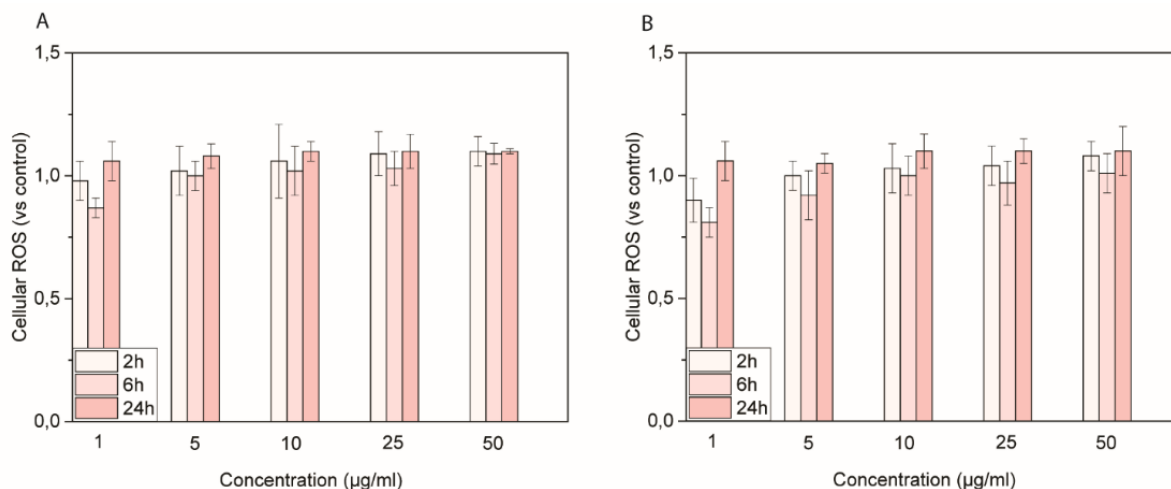


Figure 18 (A) Intracellular ROS production in NIH 3T3 cells and (B) MCF7 cells treated with different concentrations (1, 5, 10, 25 and 50 µg mL<sup>-1</sup>) of CaCO<sub>3</sub> NPs for 2, 6 and 24 h revealed using the DCFH-DA assay. The ROS increase was calculated as mean slope per mi

Moreover, we evaluated the possible DNA damage induced by CaCO<sub>3</sub> NPs using the cell comet assay. NIH 3T3 and MCF7 cells were treated with 1, 5, 10, 25 and 50 µg mL<sup>-1</sup> of CaCO<sub>3</sub> NPs for 6 and 24 h. No significant DNA damage was detected for all these concentrations at both time points in NIH 3T3 cells (Figure 19A). Similar results were obtained for MCF7 cells (Figure 19B).

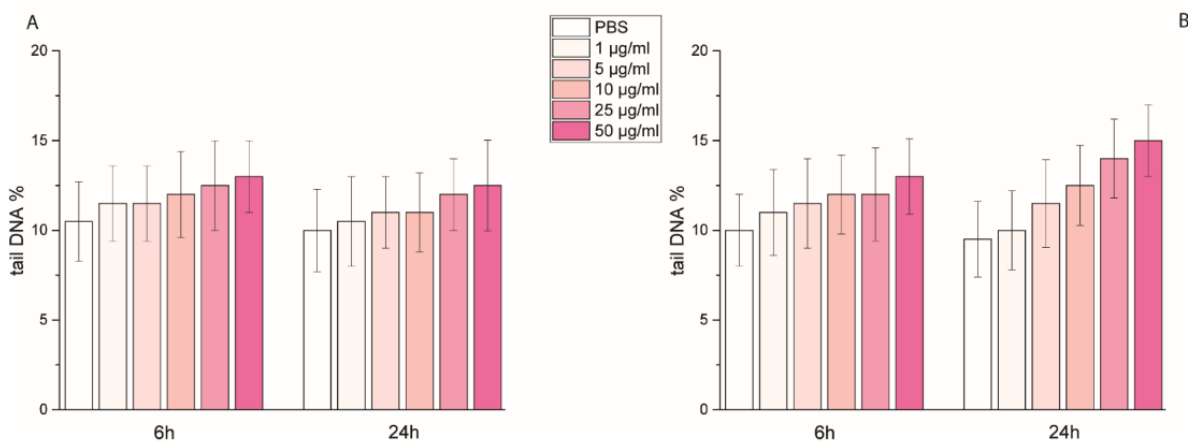



Figure 19 Percent of DNA in the tail (tail DNA%) was used as marker of DNA damage in (A) NIH 3T3 cells and (B) MCF7 cells.

All the *in vitro* studies performed to assess the impact of CaCO<sub>3</sub> NPs on cells, have demonstrated the high biocompatibility of these particles. However, since the use of CaCO<sub>3</sub> NPs will lead to human exposure, a risk assessment in a complex model organism is needed. To this end, we used zebrafish (*Danio rerio*), as vertebrate systems to investigate the biological consequences of CaCO<sub>3</sub> NPs during the development. Zebrafish, thanks to their peculiarities, including low cost, high fecundity and quick growth

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allow the *in vivo* high-throughput screening of different nanomaterials. We exposed zebrafish embryos to different concentrations of CaCO<sub>3</sub> NPs (10, 50, 100 and 200 µg mL<sup>-1</sup>) and we investigated different toxicological parameters, including the survival and hatching rates, cardiac and swimming activities and induced embryos/larvae abnormalities at several stages of growth (4, 24, 48, 72, 96 and 120 hours post fertilization). As shown in Figure 20, the survival and hatching rates presented no significant changes compared to the values of the control samples (treated only with fresh zebrafish medium) for all the concentrations tested and for all the temporal window considered. In accordance with the normative law (OECD guidelines), the values of survival and hatching rates of zebrafish embryos and larvae exposed to CaCO<sub>3</sub> NPs (10-200 µg mL<sup>-1</sup>), indicated that they were not toxic.

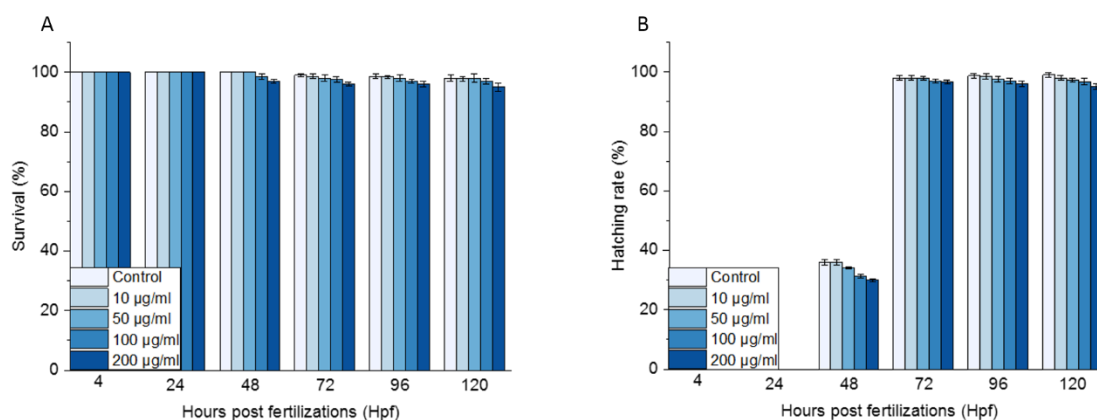



Figure 20 Survival (A) and hatching rates (B) of zebrafish exposed to different concentrations of CaCO<sub>3</sub> NPs. Data are expressed as means ± standard deviations from three independent experiments; n=80 (\*p≤0.01 in comparison to the control).

Moreover, the cardiac and swimming activities of larvae of 72 hours post fertilization (hpf) were estimated. The number of heartbeats in one minute and frequency of stimulated tail movements (Figure 21) were regular and comparable to the same parameters of untreated larvae.

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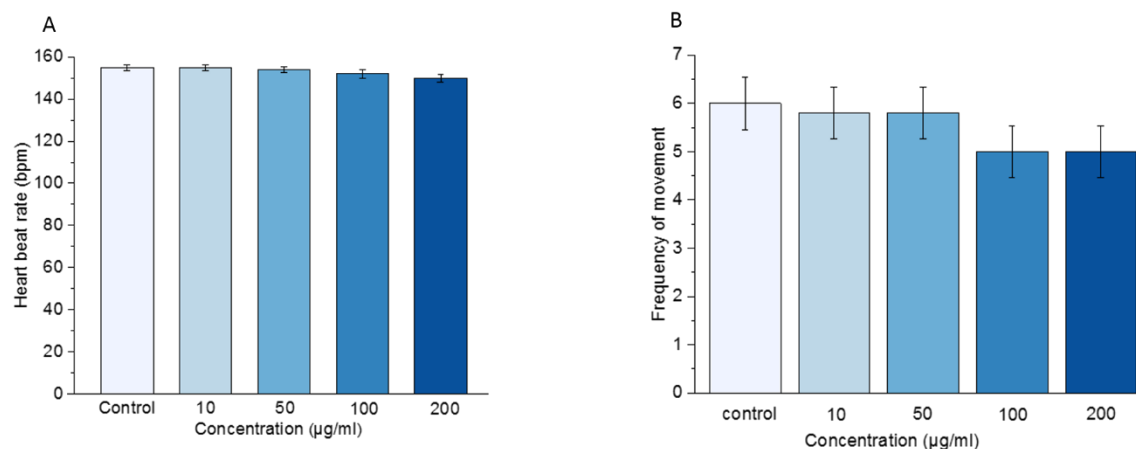


Figure 21 (A) Cardiac and (B) swimming activity of zebrafish exposed to different concentrations of  $\text{CaCO}_3$  NPs. Data are expressed as means  $\pm$  standard deviations from three independent experiments;  $n=80$  (\* $p \leq 0.01$  in comparison to the control).

Finally, we evaluated the abnormalities induced by the exposure of different concentrations of  $\text{CaCO}_3$  NPs on completed developed zebrafish larvae (96 hpf). Treated larvae presented different malformations, including finfold flexure (FF), tail flexure (TF), yolk sac edema (YSE) and pericardial edema (PCE) (Figure 20). However, the percentages of incidence of these defects were low and negligible (<4%) (d'Amora et al., in preparation).

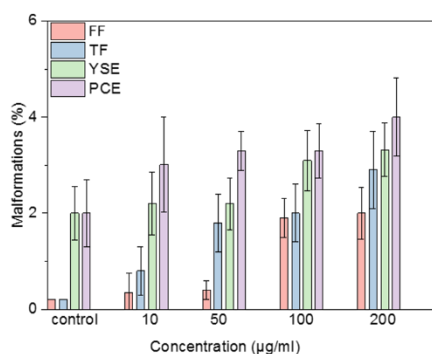



Figure 22 Histograms of percentage of each larvae defect versus  $\text{CaCO}_3$  NPs concentrations. Data are expressed as means  $\pm$  standard deviations from three independent experiments;  $n=80$  (\* $p \leq 0.01$  in comparison to the control).

Our assessments of the different toxicological endpoints demonstrated that  $\text{CaCO}_3$  NPs do not interfere with zebrafish development and possess high biocompatibility in these vertebrates systems. These findings are in good agreement with our previous findings in different cell lines. Our results can be used

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to predict the possible effects of  $\text{CaCO}_3$  NPs in humans, thanks to the high similarity, in particular in terms of the genome, between zebrafish and humans.

## 4 Findings and next steps


Within the RECODE project a preliminary LCA was calculated. These results suggest that the absorption and desorption unit is the only point in RECODE in which  $\text{CO}_2$  emissions are negative. Thus, improving this unit will improve the overall plant. Compression and dissolution piston save around 40% of energy with respect to a conventional compression. This fact makes the environmental footprint of this unit dominated by the compressed materials and not by the energy as could be expected. The simultaneous  $\text{CaCO}_3$  and  $\text{NH}_4\text{Cl}$  production from  $\text{CaCl}_2$  gets better results than the single production of  $\text{CaCO}_3$  from  $\text{CaO}$ . The design of electrochemical reactors is still being defined. Hence, the environmental impacts of their products should be updated.

The projected energy recovery will be implemented in the next update of the LCA model. As soon as the developments will be ready, by quantifying how much energy is expected to be recovered by the low-grade heat sink, LCA team will evaluate the final environmental footprint. Environmental Impacts will lower if this item is able to recover as much energy as possible.

Further data collection is required to determine exactly how raw materials and energy affects the environmental impacts. Under optimal loading within the cement, the  $\text{CaCO}_3$  nanoparticles should enable a performance increase of the concrete in terms of mechanical properties, non-permeability to chlorides, hydration behaviour, etc. such that >5% cement savings could be achieved in concretes. This mass recovery will be introduced in a new cement cycle production. This kind of loops will decrease the environmental footprint of RECODE and it will be available in the final LCA Deliverable.

Finally, within the RECODE project a REACH analysis has been also conducted. Information about properties and hazards of all substances involved in the project were collected and assessed in order to managing the risk posed by those and providing appropriate safety information for the consortium and other users. The REACH regulation was studied and presented to the consortium during the first meetings.




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Flue gas and CO<sub>2</sub>, main input of the RECODE plant are covered by Annex IV and V of the REACH and are exempted from the following Parts of REACH:


- Annex IV: Titles II (registration), Title V (downstream user regulation), Title VI (evaluation) and Title VIII (Authorization),
- Annex V: Title II (Registration); Title V (Downstream Users); Title VI (Evaluation).

This means that, their registration in the ECHA database is deemed inappropriate or unnecessary. Thus, in case of commercializing the technology, those are not required to be registered in the central database in the ECHA, but appropriate information to show that the substances qualify for the exemption must be provided to the authorities (on request). However, the registration of some products and chemicals is required. Furthermore, all the plant sub-units were studied and analysed and information about hazards and properties of the substances were provided by the partners responsible and those are reported in this deliverable. Additionally, the toxicity assessment of a specific product of the RECODE process, namely CaCO<sub>3</sub> nanoparticles, was performed through different *in vitro* and *in vivo* screenings. It was demonstrated the high biocompatibility in specific target cells of the CaCO<sub>3</sub> nanoparticles as well as their high biocompatibility in selected vertebrates systems (zebrafish, very similar to humans in terms of genome), allowing to predict the absence of health and safety effects of CaCO<sub>3</sub> NPs in humans.

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