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Recycling CO₂ from flue gas for CaCO₃ nanoparticles production as cement filler: A Life Cycle Assessment.

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Abstract

CaCO₃ nanoparticles as filler have received considerable attention for the mechanical improvement that they provide to cements. However, their life-cycle impact on the environment remains almost unexplored, even if the cement industry is considered one of the largest CO₂ emitters. In this perspective, this research work assessed a novel method for using CO₂ from cement flue gases to produce nanoCaCO₃ as cement filler within the cradle to cradle thinking. For this purpose, two routes of CO₂ capture were assessed followed by the study of the synthesis of CaCO₃ through a mineral carbonation. Three scenarios for the synthesis of CaCO₃ nanoparticles were assessed targeting the use of waste or by-products as raw materials and recirculation of them to reduce any kind of emission. The three scenarios were evaluated by means of the Life Cycle Assessment methodology. Once the best considered route for nanoCaCO₃ production was determined, this research work examined the environmental effect of including 2 wt% of CaCO₃ nanoparticles into the cement. Closing the loop follows a circular economy approach since the CO₂ is captured within the same cement factory. The results were compared with conventional Portland cement. Regarding nanoCaCO₃ results, the scenario with simultaneous production of NH₄Cl, and using as calcium source CaCl₂ deriving from the soda ash Solvay process, proved to be the best option. Moreover, when cement was filled with 2 wt% of this nanoCaCO₃, the benefit in terms of emission reductions in the Climate Change category was higher than 60% compared to the conventional Portland cement.

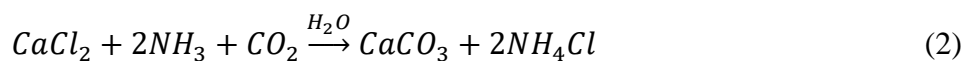
Keywords: Life Cycle Assessment (LCA); Cradle to cradle; Carbon Capture and Utilization (CCU); Mineral carbonation; Portland Cement

1. Introduction

The cement industry produces more than 5% of global anthropogenic CO₂ emissions, as well as SO₂, NO_x and other pollutants [1]. The cement industry is characterized by several sources of CO₂ emissions, spanning from the raw material extraction to the production or even the transportation of the final product. In particular, the main sources of CO₂ emissions are concentrated in the production phase, and they mainly derive from the fuel burning associated with the heating process of the raw material, and in its consequent thermal decomposition into metal oxides. The emissions largely depend on the raw material composition, the fuel and the efficiency of the process. Therefore, the carbon footprint of the cement industry varies significantly from plant to plant. Other emissions are negligible compared to the above.

Recently, Carbon Capture and Storage (CCS) and Carbon Capture and Utilization (CCU) became a major interest for climate change mitigation. In this respect, the flue gases of the cement industry have a great Carbon Capture and Utilization (CCU) potential since their typical CO₂ content is 14-33% w/w [2]. Several technologies are employed to capture and convert CO₂ into added value products. In fact, CO₂ is widely employed to produce fuels, polymers, chemicals, inorganic carbonates, etc. Biodiesel, methanol and ethanol are among the most common fuels produced through CCU technologies [3,4]. Regarding the CO₂-derived products for non-energy use, the most relevant compounds in the polymer field are polycarbonates, polyols and resins, while formic acid and isopropanol are the most significant chemicals. In line with this, inorganic carbonates like magnesium carbonate and calcium carbonate can be produced through mineral carbonation. Magnesium and calcium are widely available in nature in the form of silicate minerals such as wollastonite, serpentine, etc. [3,5]. Mineral carbonation is a chemical process in which CO₂ reacts with a metal oxide, such as magnesium or calcium to form carbonates [3]. The advantage lies in the fact that the production of stable carbonates provides long term CO₂ storage [3,6].

CaCO₃ nanoparticles are widely used as fillers to improve the mechanical properties of materials like polymers and cement [7,8]. The production of CaCO₃ nanoparticles through carbonation is therefore a very interesting alternative for CO₂ emissions mitigation. In this research work, the synthesis of CaCO₃ particles was studied through mineral carbonation in a Packed Bed Reactor (PBR). This approach guarantees control of the particle growth and agglomeration and aims to obtain nanosized particles. Therefore, this research work assesses the production of CaCO₃ nanoparticles by the implementation of a PBR by considering two different routes. In the first route, CaCO₃ is produced using a waste CaO as the source of calcium, which for instance may come from the purification of steelmaking slags; whereas, in the second route, CaCO₃ is produced by means of CaCl₂ and NH₃. This case also uses a low value calcium source, like calcium chloride, which is the by-product of the soda ash Solvay production process. The two routes follow the reactions (1) and (2), respectively, reported below.



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2. Material and methods

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2.1 Goal and scope Definition

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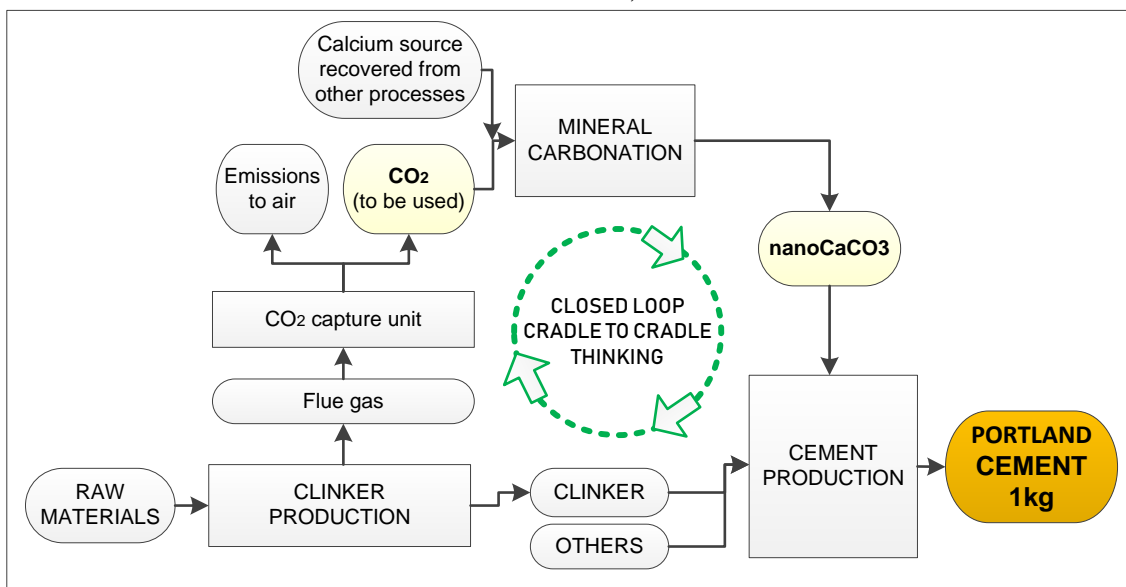


Figure
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Table

		IL	MEA	Units
CO ₂		61	93.3	kg/h
Inputs	Dataset			
Electricity	Electricity,	109.64	9.46	kWh
Thermal	Heat,	172.26	393.75	kWh
Ionic	Ionic	13		kg/h
MEA	Monoethanolamine		150	kg/h
Water	Water,		0.68	kg/h
CO ₂	Negative	-	-	kg/h

Table

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Scenario I follows reaction $CaO + CO_2 \xrightarrow{H_2O} CaCO_3$ (1)

using CaO while Scenario II follows reaction $CaCl_2 + 2NH_3 + CO_2 \xrightarrow{H_2O} CaCO_3 + 2NH_4Cl$ (2) with CaCl₂ as calcium source. Scenario III involves

an internal recycle of CO₂ within the reactive route $CaCl_2 + 2NH_3 + CO_2 \xrightarrow{H_2O} CaCO_3 + 2NH_4Cl$ (2) to foster carbonation and reach a greater CO₂ utilization factor.

¡Error! No se encuentra el origen de la referencia. represents a simplified flowchart of the three nanoCaCO₃ scenarios. For the sake of simplicity, not all the considered items are represented in the figure (e.g. energy consumption and all emissions are not included but do considered in the assessment).

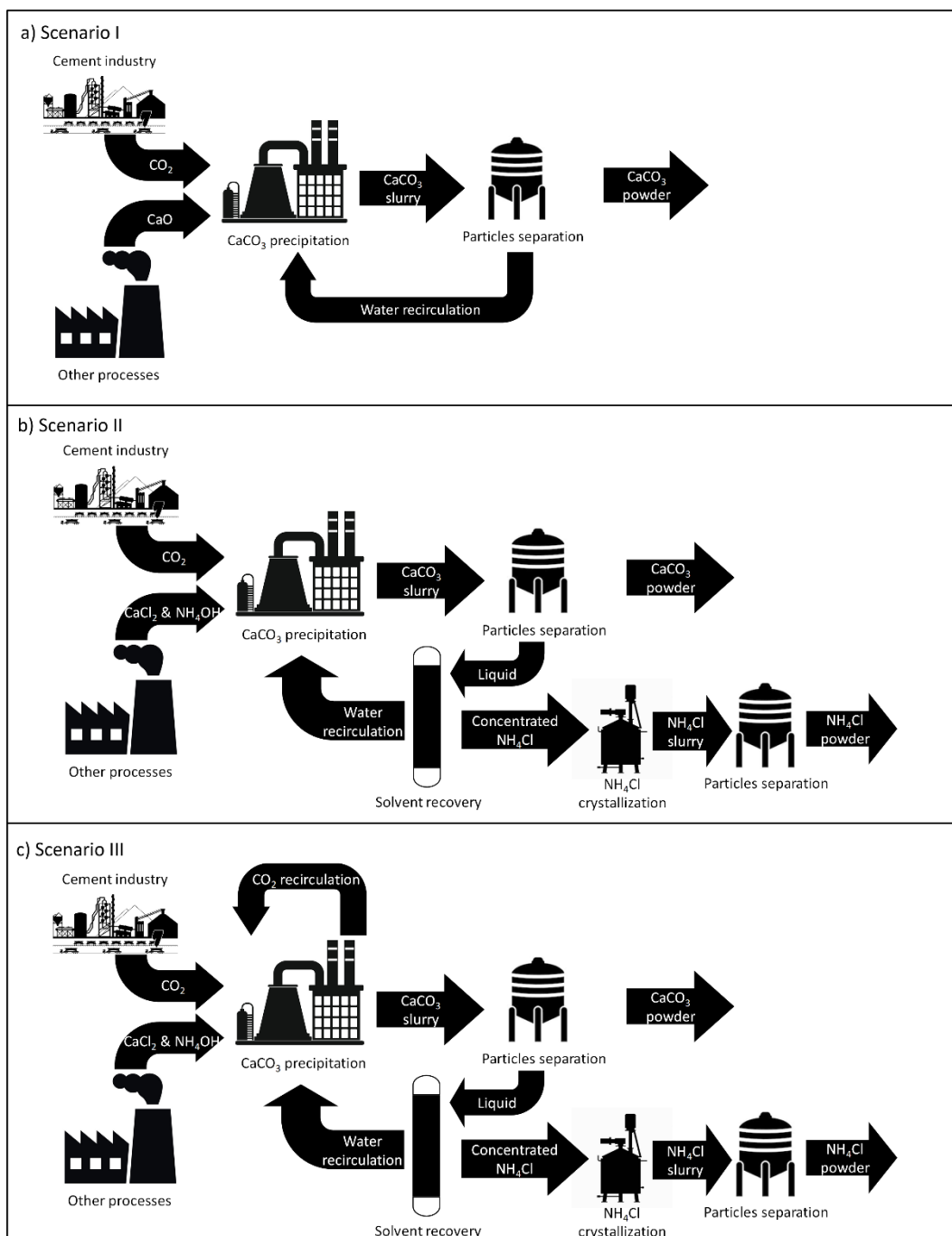


Figure 2. Process flow diagrams of the different alternatives. a) Scenario I: CaCO₃ production through carbonation of a CaO slurry. b) CaCO₃ production through carbonation of a CaCl₂/NH₄Cl solution. c) CaCO₃ production through carbonation of a CaCl₂/NH₄Cl solution with a CO₂ recycle.

First of all, the scenarios I and II were studied and optimized at lab scale according to the preparation method performed by d'Amora et al., 2020. In the case of the use of CaCl₂, an initial concentration of NH₄OH equal to 0.9 mol/L was employed. In these conditions, up to 85 and 25% of Ca²⁺ and CO₂ yields were obtained respectively. Figure 3 shows the characterization of the obtained particles in the optimal conditions in both scenarios. Starting from CaO (Scenario I) cubic nanoparticles were obtained, as shown in the FESEM micrographs (see Figure a). This is the classical morphology of calcite particles,

which is the only crystalline phase present according to the XRD spectra (see Figure d). Calcite is the most stable phase of the CaCO_3 crystalline phases at any temperature [7,26,27]. On the other hand, the presence of NH_4^+ ions in solution led to obtain mainly vaterite submicron spherical which is stabilized by the NH_4^+ ion [28] with a low content of calcite cubic particles in the scenario II, according to the FESEM micrograph and the XRD spectra (see Figure b and d). Furthermore, Figure c shows the Particle Size Distribution (PSD) for both scenarios. These particles differ in morphology and size; hence they can be different effect as filler on cement. CaCO_3 nanoparticles do not present any toxicity to the humans [25], so they are very attractive to be used in the cement, since it has to be manipulated by operators.

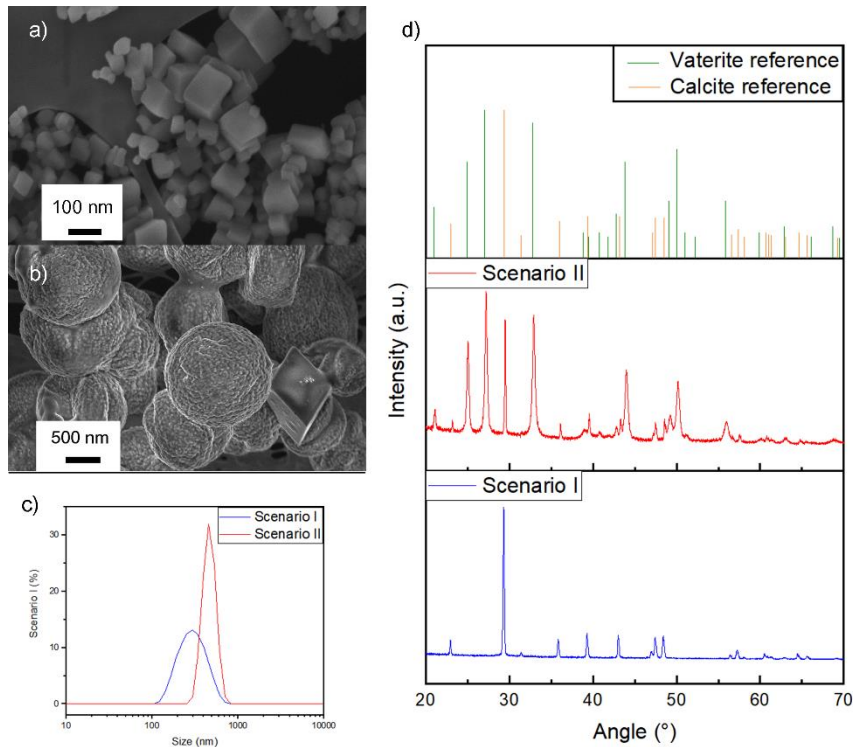


Figure 3. Characterization of Particles obtained with the PBR in scenarios I and II. a) FESEM micrographs for scenario I. b) FESEM micrograph for scenario II. c) Particle Size Distribution (PSD). D) XRD spectra.

The processes were theoretically scaled-up from the lab scale operating conditions stated by [25]. More details of these procedure regarding particles separation, filtration, crystallization, ionic exchange and energy consumption are shown in the Supplementary Material. By this procedure, the inputs and outputs for the different scenarios were determined. Table 3 summarizes the consumption and production of materials, emissions and energy consumption. The energy consumption is detailed by reporting the energy consumptions zone by zone for every scenario. This data was employed for the LCA calculations.

Table 2. Detailed energy consumptions zone by zone in every scenario.

Zone	Scenario I	Scenario II	Scenario III
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Raw material preparation	Stirring (kWh/kg CaCO ₃)	0.27	Stirring (kWh/kg CaCO ₃)	0.27	Stirring (kWh/kg CaCO ₃)	0.27
	Feeding pump (kWh/kg CaCO ₃)	0.5	Feeding pump (kWh/kg CaCO ₃)	0.67	Feeding pump (kWh/kg CaCO ₃)	0.67
	Recirculation pump (kWh/kg CaCO ₃)	0.017	Recirculation pump (kWh/kg CaCO ₃)	0.023	Recirculation pump (kWh/kg CaCO ₃)	0.023
	TOTAL (kWh/kg CaCO₃)	0.308	TOTAL (kWh/kg CaCO₃)	0.32	TOTAL (kWh/kg CaCO₃)	0.32
Precipitation zone	Stirring (kWh/kg CaCO ₃)	0.60	Stirring (kWh/kg CaCO ₃)	0.75	Stirring (kWh/kg CaCO ₃)	0.75
	Compressor (kWh/kg CaCO ₃)	0	Compressor (kWh/kg CaCO ₃)	0.00	Compressor (kWh/kg CaCO ₃)	0.077
	Pump (kWh/kg CaCO ₃)	2.04	Pump (kWh/kg CaCO ₃)	2.04	Pump (kWh/kg CaCO ₃)	2.04
	TOTAL (kWh/kg CaCO₃)	2.21	TOTAL (kWh/kg CaCO₃)	2.33	TOTAL (kWh/kg CaCO₃)	2.4
NH ₄ Cl crystallization	Column feeding pump (kWh/kg CaCO ₃)	0	Column feeding pump (kWh/kg CaCO ₃)	0.75	Column feeding pump (kWh/kg CaCO ₃)	0.75
	Column regeneration pump (kWh/kg CaCO ₃)	0	Column regeneration pump (kWh/kg CaCO ₃)	0.023	Column regeneration pump (kWh/kg CaCO ₃)	0.023
	Stirring NH ₄ Cl (kWh/kg CaCO ₃)	0	Stirring NH ₄ Cl (kWh/kg CaCO ₃)	0.93	Stirring NH ₄ Cl (kWh/kg CaCO ₃)	0.93
	Oven NH ₄ Cl (kWh/kg CaCO ₃)	0	Oven NH ₄ Cl (kWh/kg CaCO ₃)	1.57	Oven NH ₄ Cl (kWh/kg CaCO ₃)	1.57
	Pre-Column stirring (kWh/kg CaCO ₃)	0	Pre-Column stirring (kWh/kg CaCO ₃)	0.09	Pre-Column stirring (kWh/kg CaCO ₃)	0.09
	TOTAL (kWh/kg CaCO₃)	0.000	TOTAL (kWh/kg CaCO₃)	2.97	TOTAL (kWh/kg CaCO₃)	2.97
CaCO ₃ separation	Oven CaCO ₃ (kWh/kg CaCO ₃)	1.57	Oven CaCO ₃ (kWh/kg CaCO ₃)	1.41	Oven CaCO ₃ (kWh/kg CaCO ₃)	1.41
	TOTAL (kWh/kg CaCO₃)	1.57	TOTAL (kWh/kg CaCO₃)	1.41	TOTAL (kWh/kg CaCO₃)	1.41
GLOBAL ENERGY CONSUMPTION	Scenario I (kWh/kg CaCO₃)	4.08	Scenario II (kWh/kg CaCO₃)	7.03	Scenario III (kWh/kg CaCO₃)	7.1

Taking into account all the above-mentioned considerations, the Life Cycle Inventory of the three nanoCaCO₃ production scenarios was constructed. Table 3 shows the inventory of nanoCaCO₃ production per kg since we follow the Ecoinvent model that provides every mass-based process per kg. Hence, authors consider that the fact of having CaCO₃ inventory per kg production is a very illustrative option. LCI management will be latter performed by using Simapro 9 software. Hence, once the LCA of the cement will be performed, the software will allocate the impacts only to the amount of nanoparticles corresponding to the 2% w/w in the cement. As previously discussed, it is necessary first to capture the CO₂ from the flue gas and then it could be used to produce CaCO₃ nanoparticles. To get the most sustainable result as possible, the CO₂ used for that purpose will be the best option among IL and MEA carbon capture processes. As it will be showed in the Results and Discussion section, IL process is more environmentally friendly than the MEA process. Therefore, the CO₂ from IL will be part of our further nanoCaCO₃ production.

Table 3. Life Cycle Inventory of the CaCO₃ production cases of study. For the shake of simplicity, all values are referred to 1kg of CaCO₃ production.

Scenario I			Scenario II			Scenario III		
Products	Amount		Products	Amount		Products	Amount	
CaCO ₃	1 kg		CaCO ₃	1 kg		CaCO ₃	1 kg	
Expanded system								
Substance	Dataset	Amount	Substance	Dataset	Amount	Substance	Dataset	Amount
			NH ₄ Cl	Ammonium chloride {GLO} production Alloc Def, U	3.43 kg	NH ₄ Cl	Ammonium chloride {GLO} production Alloc Def, U	3.43 kg
CaO	Quicklime, milled, packed {GLO} market for Alloc Def, U	0.66 kg	CaCl ₂	Calcium chloride {RER} epichlorohydrin production from allyl chloride Alloc Def, U	1.47 kg	CaCl ₂	Calcium chloride {RER} soda production, solvay process Alloc Def, U	1.47 kg
Materials/fuels								
Substance	Dataset	Amount	Substance	Dataset	Amount	Substance	Dataset	Amount
CO ₂	CO ₂ from absorption and purification unit (Modelled)	1.33 kg	NH ₃	Ammonia, liquid {RER} ammonia production, steam reforming, liquid Alloc Rec, U	0.8 kg	NH ₃	Ammonia, liquid {RER} ammonia production, steam reforming, liquid Alloc Rec, U	0.8 kg
H ₂ O	Water, deionised, from tap water, at user {Europe without Switzerland} market for water,	5.0 kg	CO ₂	CO ₂ from absorption and purification Unit (Modelled)	2.45 kg	CO ₂	CO ₂ from absorption and purification unit (Modelled)	0.54 kg

	deionised, from tap water, at user Alloc Rec, U							
			H₂O	Water, deionised, from tap water, at user {Europe without Switzerland} market for water, deionised, from tap water, at user Alloc Rec, U	12.80 kg	H₂O	Water, deionised, from tap water, at user {Europe without Switzerland} market for water, deionised, from tap water, at user Alloc Rec, U	12.80 kg
			HCl	Hydrochloric acid, without water, in 30% solution state {RER} market for Alloc Def, U	1.87 kg	HCl	Hydrochloric acid, without water, in 30% solution state {RER} market for Alloc Def, U	1.87 kg
Electricity/heat								
Energy	Electricity, medium voltage {Europe without Switzerland} market group for Alloc Def, U	4.08 kWh	Energy	Electricity, medium voltage {Europe without Switzerland} market group for Alloc Def, U	7.03 kWh	Energy	Electricity, medium voltage {Europe without Switzerland} market group for Alloc Def, U	7.10 kWh
Emissions to air								
H₂O	Water	2.52 kg	CO₂	Carbon dioxide	2.01 kg	CO₂	Carbon dioxide	0.10 kg
CO₂	Carbon dioxide	0.89 kg	H₂O	Water	4.70 kg	O₂	Oxygen	0.09 kg
Emissions to water								
H₂O	Waste water	2.5 kg	H₂O	Waste water	5 kg	H₂O	Waste water	5 kg

2.2.2.1 Allocation procedure for nanoCaCO₃ production.

When a process produces several products, it is necessary to determine how the resources and emissions are partitioned over these coproducts. This is one of the most controversial issues in the LCA methodology: System expansion solves this problem since there the physical balances remain intact without artificial partitioning [29]. Therefore, in this research study the system expansion approach has been considered avoiding any form of allocation. The expanded boundaries here considered are explained as follows.

Calcium sources are considered from waste recovery. As showed in Table 3, Scenario I reflects that CaO could be considered as an avoided product since this could come from waste such as steel slag. Hence, the fact of using CaO from waste avoids the production of CaO as a chemical. Clearly, the use of this kind of waste could affect the process yield which will be considered in the sensitivity study shown in this paper. If the process uses CaO from waste, it is possible to consider that it is not necessary to produce it on purpose (although, for the sake of correctness, an impact on steel slag purification to obtain pure

CaO would have to be accounted for, but it was not included in this work). Likewise, for Scenarios II and III, CaCl₂ will not be introduced as a chemical but considering the recovery of CaCl₂ from its coproduction in the Solvay process as it provides a product with similar specifications to the commercial CaCl₂ [30]. Furthermore, the simultaneous production and crystallization of NH₄Cl is of interest since this extra added-value product could be sold as fertilizer contributing to the economical sustainability of the process. Scenarios II and III produce NH₄Cl as coproduct of nanoCaCO₃ production. The fact of producing this chemical (NH₄Cl) by means of the proposed process avoids the production of NH₄Cl in other industries. Hence, all the above-mentioned assumptions compose the expanded system of our study.

2.2.3 Cement filled with nanoCaCO₃

It is known that CaCO₃ as filler improves the cement technical properties [8]. Additionally, it is widely accepted that closing production loops through circular economy approaches improves the environmental performances of products or systems [31,32]. Hence, this research work examines the consequences of inserting these nanoCaCO₃ particles in the cement itself, closing the loop in a circular thinking approach.

The produced cement in a cement plant is filled by the previously described nanoCaCO₃ which, in turn, has been produced by capturing CO₂ from the cement flue gas itself. In order to model this cement from an LCA perspective, a conventional Portland process for cement production was taken directly from Ecoinvent 3 database and adapted to our case study. The dataset selected to this aim was *Cement, Portland {Europe without Switzerland}/ production / Alloc Def, U*. This Ecoinvent process considers that 0.9025 kg of clinker is needed to produce 1kg of Portland cement. According with Cosentino et al. (2019), the cement proposed in this study is obtained by substituting 2 wt% of clinker by the synthesized nanoCaCO₃ particles in the cement. Hence, 1 kg of the new cement under study contains 0.02 kg of nanoCaCO₃ and 0.8825 kg of clinker. Those CaCO₃ nanoparticles selected to be part of the new cement will be those from Scenario III, since it will be demonstrated to be the best option in terms of LCA (see the Results and discussion section).

2.2.4 Data quality

Regarding the Scenarios for nanoCaCO₃ production, this study uses experimental data from laboratory. The CO₂ conversion of the laboratory data showed a standard deviation equal to 2.04% for Scenario I and 2.97% for Scenarios II and III. The LCA will be conducted with the CO₂ conversion average values that were 20% for scenario I and 27% for scenarios II and III. Thus, the emissions and consumptions for each scenario could vary, especially at larger scale. The standard deviation of the lab results was implemented as uncertainly, which provides a variation on some process parameters, which is reported as follows. For the three CaCO₃ production scenarios, the change on the CO₂ conversion affects the process consumption and emissions for every process as shown in **¡Error! No se encuentra el origen de la referencia.** (See Supplementary Material). Moreover, in Scenario III the differences in the flow rate that should be recirculated affect as well the energy compressor consumption. In addition, the variation of the process performance could also have a slight influence on the hardness of the wastewater, but it was not considered in this sensitivity as the concentration of ions in this system is very low.

This data of the process performance will be used to do a sensitivity of the LCA results of the three CaCO₃ scenarios. Moreover, as the cement uses part of these nanoparticles, the cement LCA results will be also examined by their sensitivity.

2.3 Life Cycle Impact Assessment (LCIA) phase

SimaPro 9.0.0.48 developed by PRé Consultants was the software used to model this study with the Ecoinvent v3.1 library. International Reference Life Cycle Data System (ILCD) Midpoint method 1.09 version was used to conduct the Life Cycle Impact Assessment (LCIA). The ILCD Midpoint method was released by the European Commission, Joint Research Center in 2012. It supports the correct use of characterization factors for impact assessment as recommended in the ILCD guidance document [33]. This LCIA method includes 16 midpoint impact categories: 1 - Climate change, 2 - Ozone depletion, 3 - Human toxicity, cancer effects, 4 - Human toxicity, non-cancer effects, 5 - Particulate matter, 6 - Ionizing radiation HH (human health), 7 - Ionizing radiation E (ecosystems), 8 - Photochemical ozone formation, 9 – Acidification, 10 - Terrestrial eutrophication, 11 - Freshwater eutrophication, 12 - Marine eutrophication, 13 - Freshwater ecotoxicity, 14 - Land use 15 - Water resource depletion, 16 - Mineral, fossil & renewable resource depletion.

After the iii) LCIA phase, the iv) Interpretation phase is accomplished in the following sections.

3. Results and discussion

3.1. CO₂ capture unit

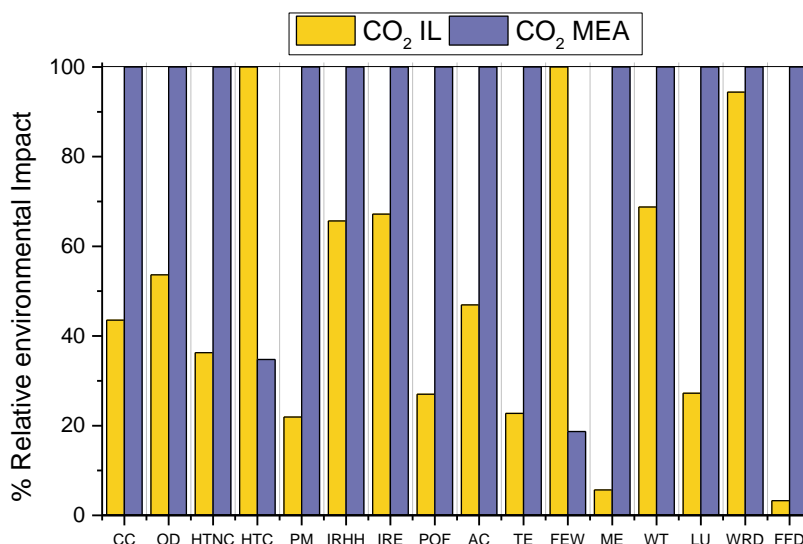


Figure 2. Comparative LCA results in relative % of impact of two CO₂ capture technologies. Absorption-desorption process by means of ionic liquid (IL) or Monoethanolamine (MEA).

Table 4. LCA Characterization results by means of ILCD method for 1kg of CO₂ captured by means of IL or MEA processes.

Impact category	Abbreviation	Unit	CO ₂ from IL process	CO ₂ from MEA process
Climate change	CC	kg CO ₂ eq	2.12	4.88

Ozone depletion	OD	kg CFC-11 _{eq}	$1.52 \cdot 10^{-7}$	$2.83 \cdot 10^{-7}$
Human toxicity, non-cancer effects	HTNC	CTUh	$1.27 \cdot 10^{-7}$	$3.51 \cdot 10^{-7}$
Human toxicity, cancer effects	HTC	CTUh	$1.14 \cdot 10^{-7}$	$3.96 \cdot 10^{-8}$
Particulate matter	PM	kg PM2.5 _{eq}	$9.90 \cdot 10^{-4}$	$4.51 \cdot 10^{-3}$
Ionizing radiation HH	IRHH	kBq U ²³⁵ _{eq}	$1.52 \cdot 10^{-1}$	$2.31 \cdot 10^{-1}$
Ionizing radiation E (interim)	IRE	CTUe	$1.13 \cdot 10^{-6}$	$1.68 \cdot 10^{-6}$
Photochemical ozone formation	POF	kg NMVOC _{eq}	$4.06 \cdot 10^{-3}$	$1.50 \cdot 10^{-2}$
Acidification	AC	molc H ⁺ _{eq}	$1.53 \cdot 10^{-2}$	$3.27 \cdot 10^{-2}$
Terrestrial eutrophication	TE	molc N _{eq}	$1.13 \cdot 10^{-2}$	$4.98 \cdot 10^{-2}$
Freshwater eutrophication	FWE	kg P _{eq}	$1.12 \cdot 10^{-3}$	$2.10 \cdot 10^{-4}$
Marine eutrophication	ME	kg N _{eq}	$1.04 \cdot 10^{-3}$	$1.84 \cdot 10^{-2}$
Freshwater ecotoxicity	WT	CTUe	2.60	3.78
Land use	LU	kg C deficit	$7.76 \cdot 10^{-1}$	2.85
Water resource depletion	WRD	m ³ H ₂ O _{eq}	3.56	3.77
Mineral, fossil and renewable resource depletion	FFD	kg Sb _{eq}	$6.72 \cdot 10^{-6}$	$2.05 \cdot 10^{-4}$

Table 4 shows the comparative LCA results for 1kg of CO₂ captured by means of IL or MEA. Furthermore, these results has been represented in Figure 2 to show their relative environmental impacts in %. Interestingly, the environmental impacts of CO₂ captured by means of IL were observed to be lower than those from MEA process in 14 out of 16 impact categories. This is a remarkable outcome. Only HTC and FEW impact categories obtained worse environmental behavior when IL are applied for capturing CO₂ instead of MEA process. Surprisingly, it is noticeable the CC impact category which shows that for capturing 1 kg CO₂ it is provoked 2.12 kg CO_{2 eq} and 4.88 kg CO_{2 eq} in the IL and MEA capturing process, respectively.

This also accords with [34] earlier observations, which showed that MEA process offers significantly higher environmental impacts than IL process. [34] also highlighted that is essentially due to the forms (and amount) of energy required, which is consistent with what we reported in Table 1. MEA process consumes 403.21 kWh (395.75 thermal kWh and 9.46 electrical kWh) for producing 93.3 kg CO₂ while IL process consumes 109.64 electrical kWh and 172.26 kWh for producing 61 kg CO₂.

Ma et al 2018., [23] was the data source for the LCA inventory of this part (Table 1). They changed the solvent in the MEA process and still operate the absorption as temperature swing adsorption (TSA). The benefit is usually only the lowered absorption enthalpy. This explains the still quite high value for thermal energy required for the IL-Scenario in Table 1.

It is known that electricity is more environmental impacting than thermal energy nevertheless, MEA process uses much more energy than IL process. The big benefit of IL with its negligible vapour pressure allows for PSA (pressure swing adsorption) mode by vacuum operation of the regeneration step. This is why the process used in the present research work (IL) operates both absorption and regeneration at more or less the same temperature, nearly isothermal. Therefore, the global MEA process environmental impacts obtained higher results due to the energy consumption and because of the use of other raw materials. For the sake of clarity, the environmental impact portion that derives from heat consumption comes from considering stand-alone columns. Obviously, in the optimized process heat integration is performed and the heat from flue gas is recovered in the CO₂ absorption-desorption unit. Hence, the heat no longer will have an impact, and consumption will be greatly reduced, and the environmental impact considerably reduced. The LCA of the optimized unit will be performed in a future development, when more reliable data about heat integration will be available.

3.2. Production of nanoCaCO₃ as cement filler

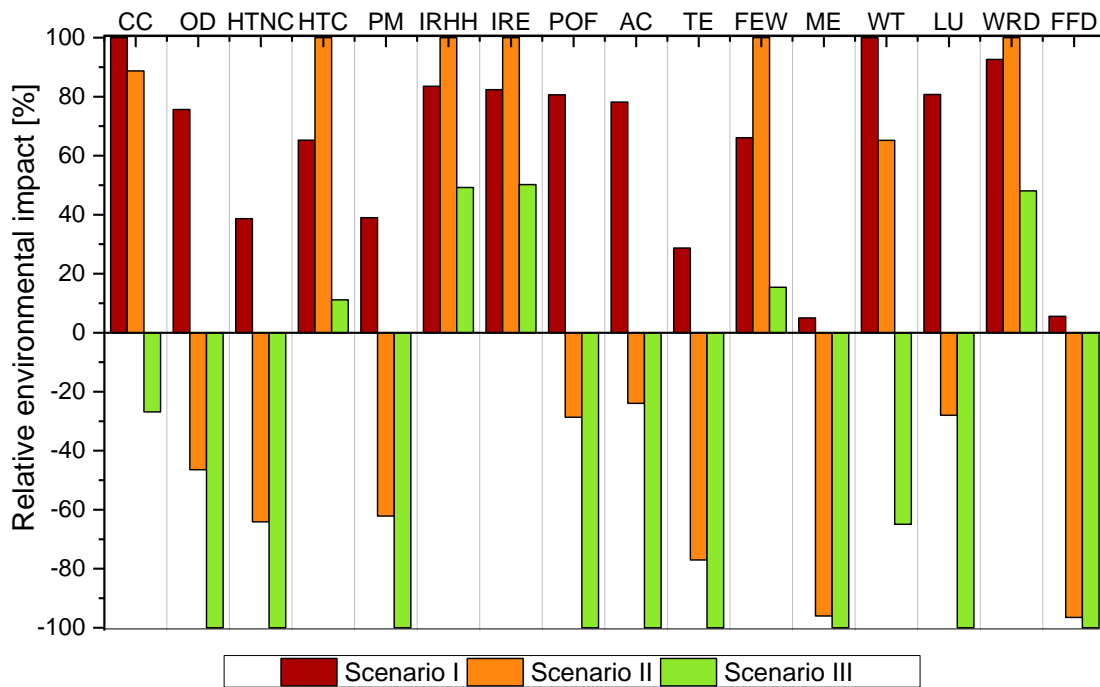


Figure 3. Comparative LCA results in relative % of impact for three different CaCO₃ production routes.

Table 5. LCA Characterization results by means of ILCD method for 1kg of CaCO₃ for the three assessed Scenarios.

Impact category	Abbreviation	Unit	Scenario I	Scenario II	Scenario III
			CaCO ₃ from CaO	CaCO ₃ from CaCl ₂	CaCO ₃ from CaCl ₂ with CO ₂ loop
Climate change	CC	kg CO ₂ eq	5.13	4.56	-1.38

Ozone depletion	OD	kg CFC-11 _{eq}	$4.04 \cdot 10^{-7}$	$-2.48 \cdot 10^{-7}$	$-5.34 \cdot 10^{-7}$
Human toxicity non-cancer effects	HTNC	CTUh	$2.61 \cdot 10^{-7}$	$-4.32 \cdot 10^{-7}$	$-6.74 \cdot 10^{-7}$
Human toxicity cancer effects	HTC	CTUh	$1.60 \cdot 10^{-7}$	$2.45 \cdot 10^{-7}$	$2.73 \cdot 10^{-8}$
Particulate matter	PM	kg PM2.5 _{eq}	$1.94 \cdot 10^{-3}$	$-3.08 \cdot 10^{-3}$	$-4.96 \cdot 10^{-3}$
Ionizing radiation HH	IRHH	kBq U ²³⁵ _{eq}	$4.70 \cdot 10^{-1}$	$5.62 \cdot 10^{-1}$	$2.77 \cdot 10^{-1}$
Ionizing radiation E (interim)	IRE	CTUe	$3.51 \cdot 10^{-6}$	$4.26 \cdot 10^{-6}$	$2.14 \cdot 10^{-6}$
Photochemical ozone formation	POF	kg NMVOC _{eq}	$8.69 \cdot 10^{-3}$	$-3.09 \cdot 10^{-3}$	$-1.08 \cdot 10^{-2}$
Acidification	AC	molc H ⁺ _{eq}	$2.99 \cdot 10^{-2}$	$-9.16 \cdot 10^{-3}$	$-3.83 \cdot 10^{-2}$
Terrestrial eutrophication	TE	molc N _{eq}	$2.67 \cdot 10^{-2}$	$-7.18 \cdot 10^{-2}$	$-9.31 \cdot 10^{-2}$
Freshwater eutrophication	FWE	kg P _{eq}	$1.67 \cdot 10^{-3}$	$2.53 \cdot 10^{-3}$	$3.90 \cdot 10^{-4}$
Marine eutrophication	ME	kg N _{eq}	$2.48 \cdot 10^{-3}$	$-4.73 \cdot 10^{-2}$	$-4.93 \cdot 10^{-2}$
Freshwater ecotoxicity	WT	CTUe	3.82	2.49	-2.48
Land use	LU	kg C deficit	1.65	$-5.71 \cdot 10^{-1}$	-2.04
Water resource depletion	WRD	m ³ H ₂ O _{eq}	11.9	12.9	6.18
Mineral fossil and renewable resource depletion	FFD	kg Sb _{eq}	$2.02 \cdot 10^{-5}$	$-3.52 \cdot 10^{-4}$	$-3.65 \cdot 10^{-4}$

A comparative LCA was carried out in order to assess the environmental impacts of the production of nanoCaCO₃ through a carbonation synthesis. The first set of results aimed to identify which of those previously described scenarios obtained lower environmental impacts. Table 5 shows their results for 1 kg nanoCaCO₃, which were calculated according to the LCA methodology explained. Figure 3 presents an overview of the differences, expressed in percentage, among the three analyzed scenarios of the nanoCaCO₃ production for all the environmental categories gathered by ILCD method. In Figure 3, the scenario with the highest environmental impact in each category is represented with 100% and the values the other scenarios are represented referred to the highest one.

The initial idea was to compare Scenario I with Scenario II in order to figure out which route was the most suitable from an LCA point of view. According to the data obtained, Scenario II showed lower values in almost all the impact categories (11 out of 16) and consequently it was decided to further improve this route by introducing a new experimental setup with the recirculation of the outlet CO₂. This is the third scenario, Scenario III.

It can be noticed from the data reported in Figure 3 and Table 5 that the nanoCaCO₃ synthesis from CaO (Scenario I) reported significantly more impacts in almost all the environmental categories with respect to the ones obtained by employing CaCl₂ as

calcium source (Scenario II and III). Scenario II improved the environmental impacts with respect to Scenario I in 11 out of 16 impact categories assessed. Only in the HTC, IRHH, IRE, FEW and WRD categories Scenario I obtained lower values than those of Scenario II. In Scenario III, the CO₂ flow rate from the absorption and desorption unit is lower than in Scenario II since part of the CO₂ from the process outlet is not emitted in air but recycled upstream the reactor. These results made Scenario III more environmentally friendly than Scenario II, since Scenario III improves all impact categories with respect to Scenario II.

One of the most striking result emerging from these data is that the CC category is reduced by 0.57 kg CO₂ per every kg of CaCO₃ produced if Scenario II is adopted instead of Scenario I (11.3% of reduction). Likewise, if Scenario III is adopted instead of Scenario I, carbon footprint (CC) is reduced by 126.8% obtaining -1.38 kg CO₂eq/kg nanoCaCO₃. Both Scenario II and III obtained negative environmental impacts in most of the impact categories. This means environmental benefits. It is important to highlight that in those categories in which Scenario II performed worse than Scenario I (HTC, IRHH, IRE, FEW and WRD), when the recirculation of CO₂ is carried out (i.e. Scenario III) positive results were obtained, being Scenario III better than Scenario I in all environmental categories.

Scenario III presented 11 impact categories in which the values were more than 100% lower than Scenario I. Besides, the reduction in the other 5 impact categories were also noticeable. Scenario III decreased their environmental impact with respect to Scenario I in HTC, IRHH, IRE, FEW and WRD were 82.9%, 41.1%, 39.1%, 79.7% and 48.1%, respectively.

It is worth to notice that Scenario II and Scenario III considered the avoided production of NH₄Cl since it is simultaneously produced with the nanoCaCO₃. In the present research work this fact influenced positively the final results since Scenario II and III obtained better results than Scenario I, globally.

Figure 3 and Table 5 revealed significant differences between the environmental impacts for 1 kg nanoCaCO₃ depending on the route used for its production. In order to highlight the contributions giving rise to these differences, a breakdown of the environmental impacts is showed in Figure 4. Figure 4 shows for all the ILCD impact categories the contributions of the different elements considered in the LCI (materials, emissions and energy) in the three nanoCaCO₃ production scenarios. It can be noticed that certain similarities can be applied for the three nanoCaCO₃ production routes.

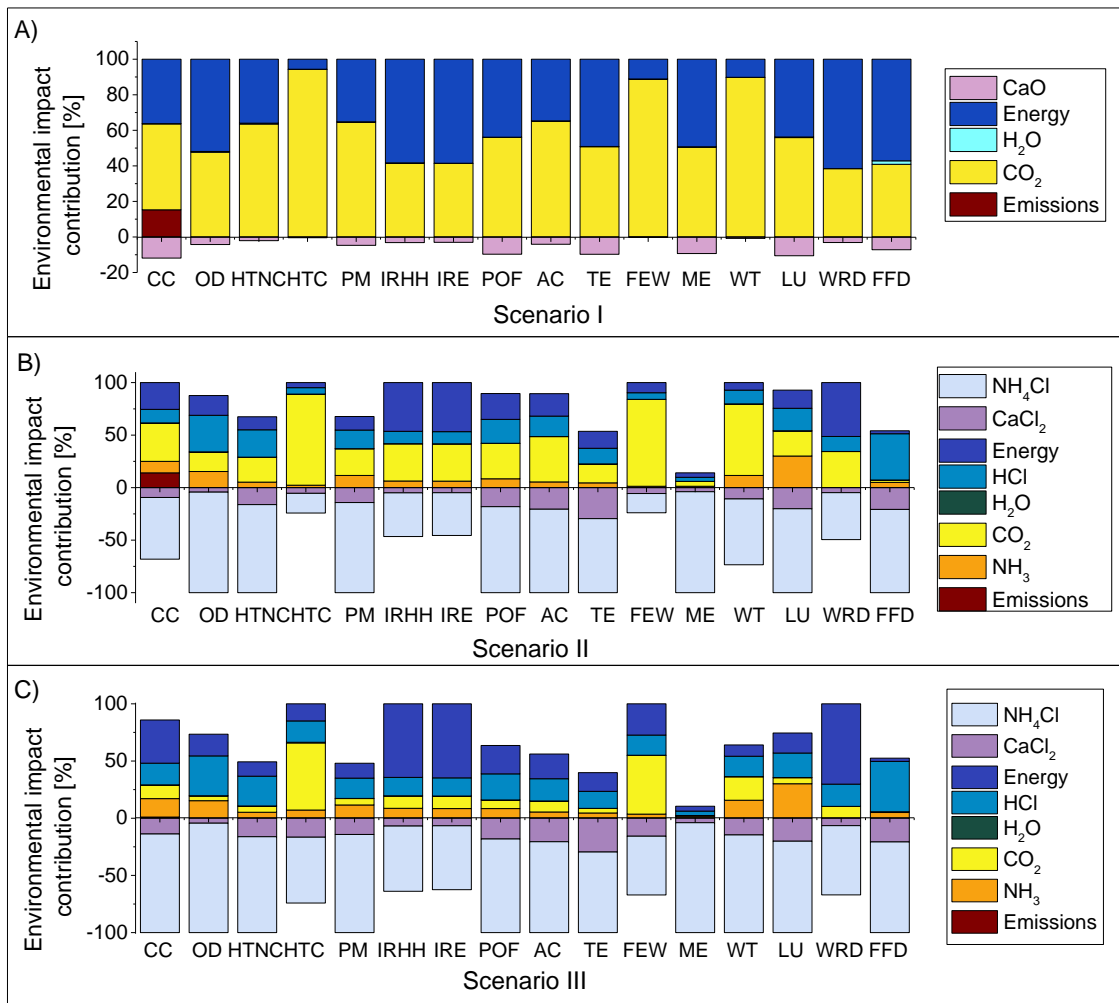


Figure 4. LCA of nanoCaCO₃. Environmental contribution to the impact categories. 2A Scenario I 2B Scenario II 2C Scenario III.

An overview of Figure 4 is helpful to understand how the impacts are composed. Figure 4 shows that in each scenario there is not a single chemical that dominates the others, but the environmental impacts are caused by the mutual contribution of several elements.

Regarding the CO₂ coming from the absorption and desorption unit, its environmental burden is carried to downstream processes that use the CO₂. Figure 4 showed this contribution as a positive value (i.e. negative connotations) for every Scenario. In fact, in Scenario I (Figure 4 a) CO₂ is the main contributor to almost all environmental categories. The most standing-out elements in Figure 4 are the negatives contribution coming from the expanded systems. In Figure 4a it is possible to notice the environmental benefits provoked by the fact of using CaO from other processes such as steel slag. This avoids its production as a chemical. Energy consumption also represents an important contribution to the environmental categories in Scenario I (Figure 4.A). For instance, energy consumption causes more than 80% of total impact in HTC, FEW and WT categories.

As far as the CC category, is concerned, Figure 3 showed that CC in Scenario I is higher than in Scenario II and III and Figure 4 shows the proportionality of these impacts. CO₂ is responsible of more than 40% of CC in Scenario I (see Figure 4 a). However, when

calcium source is CaCl_2 , the CO_2 contribution to CC is 8% and 32% for Scenario II and Scenario III, respectively (Figure 4 b c). Furthermore, the process emissions contributed for 18% in Scenario I, 14% in Scenario II and 1% in Scenario III. Therefore, it becomes clear, also in a lifecycle perspective, that the reduction of emissions contributed to decrease the Climate Change contribution. In Figure 4 c, the CO_2 contribution in Scenario III for CC is lower than Scenario II (see Figure 4 b). This is due to that Scenario III recovers part of the CO_2 emissions of Scenario II to produce nano CaCO_3 .

Several reports have shown that the addition of nano CaCO_3 increased the compressive strength of cements [35,36]. However, very little is currently known about their environmental impacts and it is still unexplored the environmental consequence of its inclusion in cements. The few studies available in the literature on the LCA of the CaCO_3 production consider other impact categories than the present study. Furthermore, as far as the authors knowledge, LCA studies about nano CaCO_3 particles are totally missing. Hence, all the indicators calculated at the present study are difficult to be compared.

The most common calcium carbonate production method is the carbonation process from limestone. Mattila et al., 2014 estimated the carbon footprint of calcium carbonate produced by the conventional way and also by an alternative method from the conversion of steel slag as calcium source instead of limestone. Their results revealed a carbon footprint around 1 kg CO_2 eq per every kg of CaCO_3 produced in the conventional way. However, when calcium carbonate was produced from steel slag, carbon footprint reached more than 3 kg CO_2 eq per kg of CaCO_3 produced. It is important to highlight that these results were not obtained for nanosized particles. The present study obtained 5.13 kg CO_2 eq, 4.56 kg CO_2 eq, and -1.38 kg CO_2 eq in Scenarios I, II, and III, respectively. These findings confirmed the order of magnitude of those obtained by Mattila et al., 2014 for the conventional route but presented considerably improved results when the system also produced NH_4Cl and part of the CO_2 emitted in the first open loop (Scenario II) is recirculated (Scenario III).

Regarding CO_2 capture and utilization, a previous study [37] exploited the properties of the reverse reaction here employed ($\text{CaCO}_3 + \text{heat} \rightarrow \text{CO}_2 + \text{CaO}$) always with the aim of carbon capture by using a CaO loop. Even if this study is devoted to different applications than ours, Zakuciová et al., (2018) highlighted the LCA as a tool to lead to the further steps towards the innovation for lowering the level of CO_2 in flue gases.

Since high sources of heat are present in the cement industry, further improvements could be achieved in this process. These hot streams could be employed in order to integrate the heat to our process, mainly for the CO_2 recovery, the particles drying and the NH_4Cl crystallization. This further optimization would surely improve these LCA results.

3.3 LCA of cement

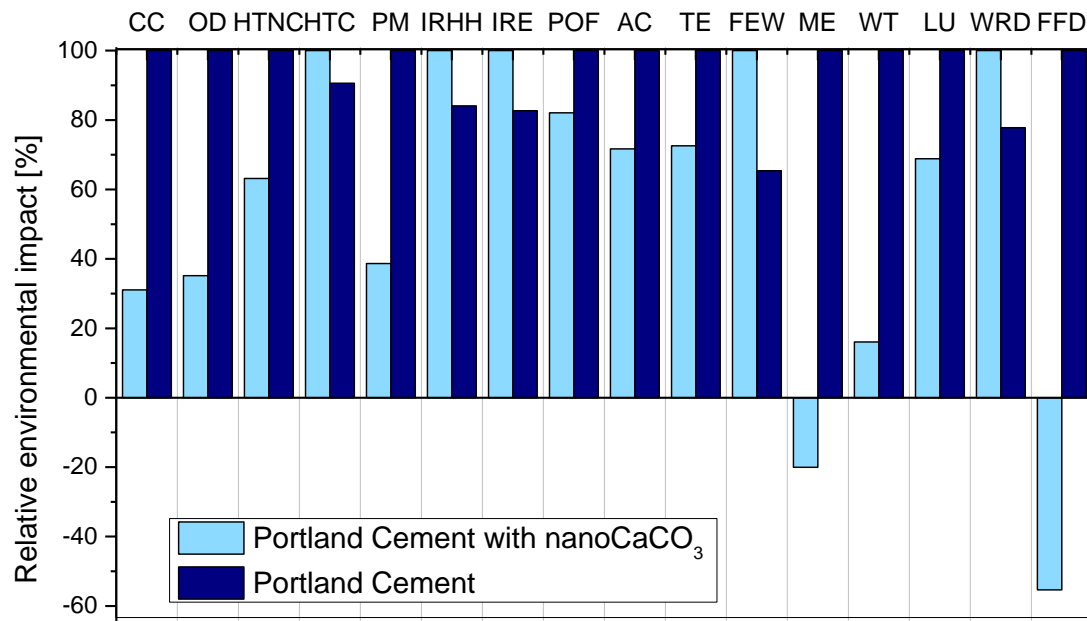


Figure 5. Comparative LCA between common cement Portland and an improved cement Portland with nanoCaCO₃ as filler.

Table 6. LCA Characterization results by means of ILCD method for 1kg of cement. A Comparison between common Portland cement and a cement with recovered nanoCaCO₃ from cement flue gases.

Impact category	Unit	Portland cement with 2 wt% CaCO ₃	Portland cement
CC	kg CO ₂ eq	$2.99 \cdot 10^{-1}$	$9.61 \cdot 10^{-1}$
OD	kg CFC-11 eq	$6.34 \cdot 10^{-9}$	$1.80 \cdot 10^{-8}$
THNC	CTUh	$2.52 \cdot 10^{-8}$	$3.99 \cdot 10^{-8}$
HTC	CTUh	$1.99 \cdot 10^{-9}$	$1.80 \cdot 10^{-9}$
PM	kg PM _{2.5} eq	$6.63 \cdot 10^{-5}$	$1.71 \cdot 10^{-4}$
IRHH	kBq U ²³⁵ eq	$2.04 \cdot 10^{-2}$	$1.72 \cdot 10^{-2}$
IRE	CTUe	$1.51 \cdot 10^{-7}$	$1.25 \cdot 10^{-7}$
POF	kg NMVOC eq	$1.98 \cdot 10^{-3}$	$2.41 \cdot 10^{-3}$
AC	molc H ⁺ eq	$2.31 \cdot 10^{-3}$	$3.22 \cdot 10^{-3}$
TE	molc N eq	$6.66 \cdot 10^{-3}$	$9.18 \cdot 10^{-3}$
FWE	kg P eq	$1.79 \cdot 10^{-5}$	$1.17 \cdot 10^{-5}$
ME	kg N eq	$-1.61 \cdot 10^{-4}$	$8.03 \cdot 10^{-4}$
WT	CTUe	$1.12 \cdot 10^{-2}$	$6.97 \cdot 10^{-2}$
LU	kg C deficit	$1.97 \cdot 10^{-1}$	$2.86 \cdot 10^{-1}$
WRD	m ³ water eq	$4.36 \cdot 10^{-1}$	$3.39 \cdot 10^{-1}$
FFD	kg Sb eq	$-2.71 \cdot 10^{-6}$	$4.90 \cdot 10^{-6}$

The CO₂ from flue gas is captured and purified and employed to produce nanoCaCO₃ which is a filler to improve the mechanical properties of the cement. The present research work also aims at investigating the environmental performance of this nanoCaCO₃-filled

cement with respect to the conventional Portland cement. Therefore, a comparative LCA between a conventional Portland cement and the cement with nanoCaCO₃ here investigated was carried out. Figure 5 illustrates the relative impacts for the two cements in all the environmental categories assessed. Table 6 reports the environmental impact results for 1 kg of the nanoCaCO₃-filled cement and the conventional Portland cement, for all the ILCD impact categories. It can be noticed from Figure 5 and Table 6 that most of the environmental categories featured better performances of the Portland cement with nanoCaCO₃ in comparison to the conventional Portland cement. Particularly in the case of the HTC, IRHH, IRE, FEW and WRD environmental categories the conventional Portland obtained better results than the 2%wt nanoCaCO₃-filled. Conversely, the situation for the CC, OD, HTNC, PM, POF, AC, TE, ME, WT, LU and FFD categories is completely reversed: all these indicators showed better environmental behavior in the case of the cement filled with the nanoCaCO₃ produced through CO₂ coming from its own flue gas. In particular, a strong and evident reduction of the environmental impact in the CC category for the nanoCaCO₃-filled cement can be appreciated. In fact, Climate change of 1 kg of Portland cement is 0.96 kg CO₂ eq while for the nano-added cement it is 0.3 kg CO₂ eq, meaning a reduction of 69% in the CC category. McDonald et al., (2019) stated that the exploitation in the cement industry of the carbon dioxide contained in the flue gas to produce calcium carbonate can reduce the carbon footprint of blended Portland cements by more than 25%. In spite of their promising results, they recommend a full LCA of calcium carbonate cements in order to get more accurate results. With this study that suggestion is fulfilled.

Jayapalan et al., (2013) studied the effect of titanium dioxide (TiO₂) and calcium carbonate nanoparticles as filler on early age properties and behavior of cement-based materials and found that these particles boost the early age hydration and increase the chemical shrinkage. The results in the POF category confirm the findings of the work of Jayapalan et al., (2013), that studied an LCA analysis for the cement added with 5% of calcium carbonate and compared it with the ordinary Portland cement paste. Their results revealed that cement with CaCO₃ nanoparticles addition utilized lower resources and obtained lower contribution to photochemical smog than the conventional Portland cement.

There is a vast amount of environmental assessment of cement [1,9,39–43]. Figure 6 provides the contribution analysis of the conventional Portland cement (Figure 6 a) and cement filled with 2 wt% of nanoCaCO₃ under investigation (Figure 6 b). As it could be noticed in Figure 6 a, in almost all the impact categories the main contribution comes from clinker, getting values higher than 90% in the CC, PM, POF, AC, TE and ME categories. These results are in line with those of the study of Marinković et al., 2013 stating that clinker is by far the largest contributor to all category indicators. The partial substitution of clinker with nanoparticles is represented in Figure 6 b. It is possible to notice how a little inclusion of CaCO₃ could considerably affect all the environmental impact categories with more emphasis in OD, PM, ME, WT and FFD.

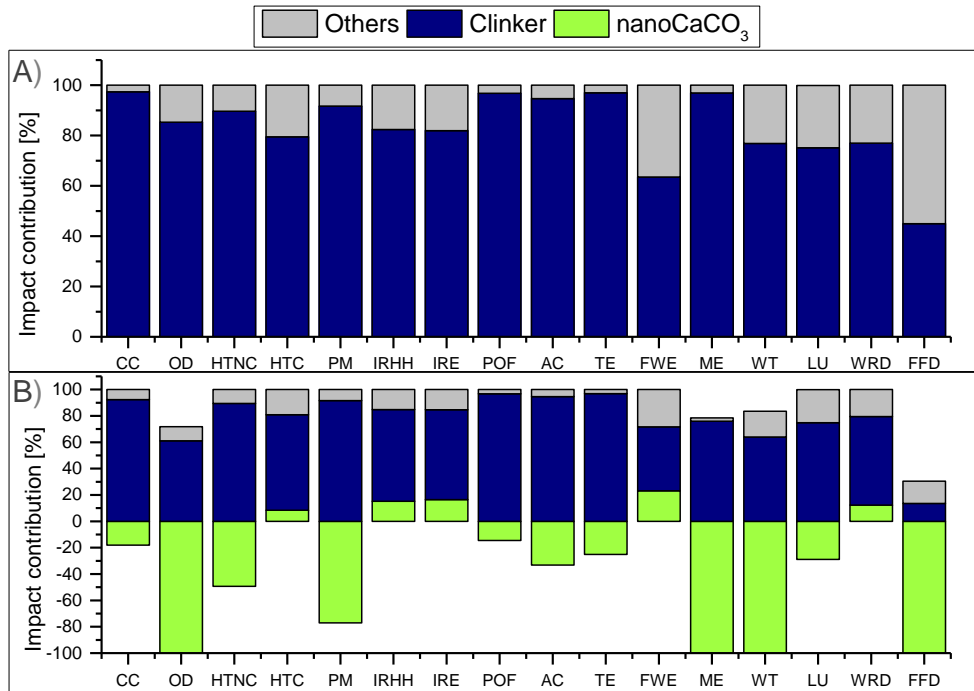


Figure 6. Environmental impact contribution [%] of the cement components. A. - Conventional Portland Cement. B. - Cement filled with nanoCaCO₃ produced with the CO₂ from flue gas from the cement production itself.

The reduction of 69% in the CC category is one of the most striking results of this research work and it is hereafter discussed. Figure 6a highlights the key role of clinker in the different impact categories, suggesting the item where it is most important to operate by reducing the environmental impacts of clinker. As explained in Figure 7 a, the cement production is a linear process. Ecoinvent database considers that 1kg clinker releases 0.839 kg CO₂ into the air. Moreover, this database considers as well that 1kg of Portland cement needs 0.902 kg of clinker. Hence, in 1 kg of conventional Portland cement the CO₂ emissions coming from clinker are 0.791 kg (Data from the LCI for the conventional Ecoinvent Portland cement process). In the present research work, knowing the mechanical properties enhancement [7,45], the authors proposed a method for closing that loop improving the environmental impacts. Figure 7 b represents a flowchart of the circular process in which it is possible to notice several environmental benefits (highlighted in green) compared to the scheme of Figure 7 a. Figure 7 b shows that the 2 wt% substitution of nanoCaCO₃ reduces the clinker needs (0.902 kg clinker in the linear process vs. 0.884 kg in the circular process). This simple action already reduces the CO₂ emissions from 0.791 to 0.742 kg CO₂ per kg of cement. It is important to highlight that this is direct emission not environmental impact. The environmental impact will be composed by these emissions all other items in the system translated into Climate Change category. Following with this discussion, if we assume a yield of 80% in the CO₂ capture, only 0.148 kg CO₂ deriving from clinker are now released into the air. Moreover, it is possible to notice in green (Figure 7 b) other downstream environmental benefits that the circularity provides to the cement production process. This is reflected in the environmental results as already explained in Table 6 in Figure 8 and Figure 9. As described before, the calcium source is a recovery from other processes such as the Solvay one. Besides producing two chemicals in the mineral carbonation process reduces the

environmental impacts as well since the coproduct can be sold or used in other cycles. Finally, the consequential approach valorizes the fact of non-disposal of waste producing environmental benefits. For all the above-mentioned questions we obtained the encouraging result for CC category in the present research work.

Sensitivity

This study indicates that the substitution of cement by 2% of so-produced CaCO₃ could reduce the emissions of the OPC production in a 69%. Furthermore, the production of CaCO₃ using calcium wastes is also economically feasible as assessed by Teir et al. [46]. They concluded that if the produced calcium carbonate can be sold to a price of 150 €/t, the investment payback time would be 2.2 years. Of course, this change from process to process. But by assuming that the price of sub micron CaCO₃ particles produced by this approach in the market can vary between 50-250 €/kg, the investment payback could be reduced. In addition, the growth on the application demand of CaCO₃ led to a significant growth in the market, and an increase on the price of CaCO₃ is expected for the next years, which indicates that the production of CaCO₃ through carbonation is a promising way to reduce CO₂ emissions and increase the process revenue [47,48]. However, this approach includes the use of CaCO₃ inside the same cement industry and not the sale of the product. Therefore, if this approach is implemented in the cement industry, the cementitious materials properties could be improved by saving a lot quantity of money after the 2 years of its implementation. However, a more detailed economic study will be done once the pilot plant will be built in the framework of the RECODE project.

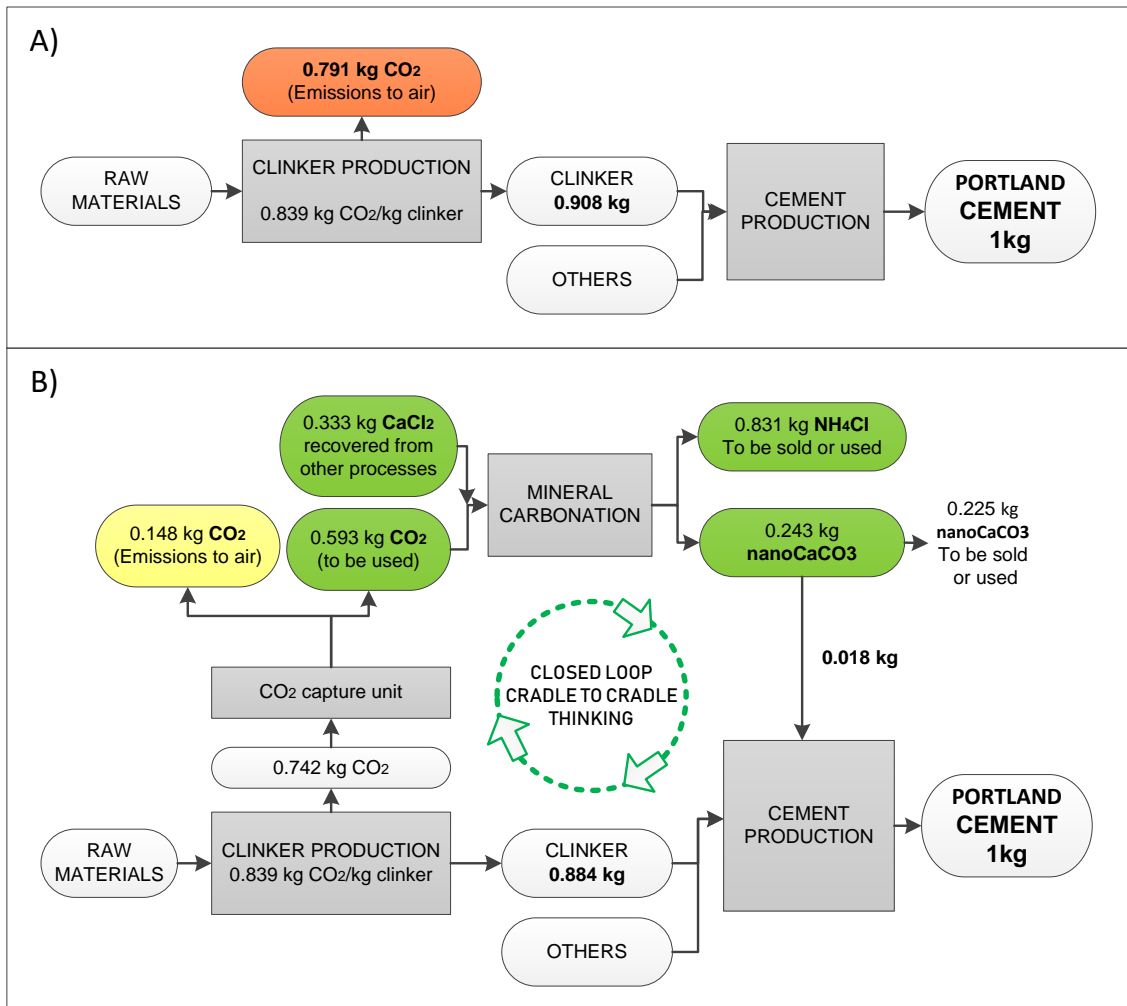


Figure 7. Hotspot and environmental benefits schemes for the Portland Cement production process. A) Conventional (linear) Portland Cement process (Data from Ecoinvent database). B) Improved (circular) cement production process by integrating the CaCO_3 nanoparticles produced from their own flue gas.

4. Conclusions

This research work was carried out to design an environmentally friendly production of CaCO_3 nanoparticles and to evaluate the environmental impacts of an innovative cement filled with these nanoparticles, in a circular economy thinking approach. The review of the literature suggested that there is an urgent need to reduce the carbon footprint of the cement industry. With this aim, CO_2 is captured from the cement flue gas and used to produce nanoCaCO_3 . Three scenarios of the nanoCaCO_3 production were assessed through LCA. In Scenario I CaO is used as calcium source while CaCl_2 is used in Scenario II. Scenario III is the same as Scenario II but with the recirculation of the CO_2 emissions.

The synthesis of CaCO_3 from CaO led to obtain cubic calcite with conversions of calcium and CO_2 equal to 85% and 42% respectively. On the other hand, regarding $\text{CaCl}_2/\text{NH}_4\text{OH}$, mainly spherical vaterite were synthesized and calcium and CO_2 conversions equal to 75% and 19% were reached respectively.

One of the most significant findings to emerge from this study is that the scenarios which employed CaCl_2 as the calcium source (II and III) obtained globally better environmental results than Scenario I. In Scenarios II and III, NH_4Cl is produced as a by-product, which

avoids its production as a chemical obtaining considerable environmental benefits. Scenario III of nanoCaCO₃ production obtained encouraging results in all the environmental categories assessed.

This study demonstrates that the partial substitution of the Portland cement with the developed CaCO₃ nanoparticles allows the reduction of the value of the Climate Change category in the cement, that is of the utmost importance in an industry in which CO₂ reduction is the main concern. In fact, the Portland cement with 2 wt% of CaCO₃ nanoparticles obtained a value of 0.3 kg CO₂ eq/kg cement whereas the conventional Portland cement obtained a value equal to 0.96 kg CO₂ eq/kg cement, with a reduction of about 69% in this category.

To the best of our knowledge, this is the first study which originally examines the complete chain constituted by the capture and purification of CO₂ from the flue gas of the cement industry, the production of CaCO₃ nanoparticles by a carbonation route and their use as a filler in cement, as well as the associations between these three processes and their environmental impacts.

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