

# Deep Decarbonization of the Cement Sector: A Prospective Environmental Assessment of CO<sub>2</sub> Recycling to Methanol

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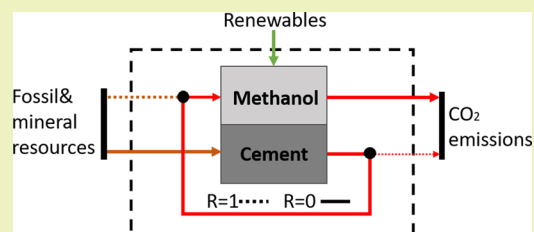


Supporting Information

**ABSTRACT:** Current decarbonization pressures are prompting efforts to reimagine the future of the hard-to-abate cement sector. To date, fuel switching has arisen as the most readily operational strategy, and its application in the cement sector is expected in the short to midterm. However, around two-thirds of the cement CO<sub>2</sub> emissions come from the calcination of limestone. The implementation of CO<sub>2</sub> capture utilization and/or storage will be crucial to support a reliable net-zero carbon future by 2050–2070. CCS is considered as the most carbon-neutral technology in the cement decarbonization roadmap, while CO<sub>2</sub> recycling (CCU) has arisen as a suitable strategy

for those locations where there is an industrial symbiosis between the cement market and CO<sub>2</sub>-based chemical markets (e.g., methanol, formic acid, etc.). Despite that the CCU strategy cannot be carbon-neutral by itself, it could be a powerful option in combination with CCS. To date, most CO<sub>2</sub> recycling technologies are still emerging, and their development has to be boosted in the next decades. In this study, a prospective environmental analysis has been conducted through life cycle thinking to explore the benefits of cement long-term decarbonization by implementing a carbon recycling plant (CRP) based on the emerging electrochemical reduction (ER) of CO<sub>2</sub> to produce methanol (MeOH). The study aims to demonstrate the synergic decarbonization and defossilization for both cement and MeOH markets, respectively. Cell energy efficiency and MeOH concentration have been identified as the key performance parameters that should be around 60% and 40% wt, respectively, to ensure a future sustainable implementation of ER to the MeOH technology. A CRP powered by low-carbon renewable electricity (<0.02 kg CO<sub>2,eq</sub>/kW h) and with a low-fossil depletion (FD) impact (<0.01 kg oil<sub>eq</sub>/kW h) could lead to an integrated cement and MeOH production with sharp reductions in the carbon footprint (~75%) and FD (~66%) of the integrated cement and MeOH production compared to the conventional fossil-based productions. The proposed CO<sub>2</sub> recycling scheme can contribute to accelerating the innovation of carbon capture and recycling technologies and their deployment in these hard-to-abate sectors.

**KEYWORDS:** carbon dioxide, decarbonization, hard-to-abate sectors, cement production, electrochemical reduction, CO<sub>2</sub> capture, methanol



## INTRODUCTION

One of the top carbon dioxide (CO<sub>2</sub>) sources is the production of cement, an important binding material around the world. Within this hard-to-abate sector, CO<sub>2</sub> is mainly released by the reactions involved in clinker production, whereas fuel combustion, generally coal, petcoke, and natural gas, entails the remnant CO<sub>2</sub> direct emissions (~30%). Given the cement-demographic nexus, the production of this binding material accelerated rapidly worldwide, increasing 50-fold since 1950. The global capacity reached 4.1 Gt in 2019, and it is expected to grow moderately to 2030.<sup>1</sup> Since the Paris Agreement, the urge for implementing innovative carbon recycling technologies in these sectors has become more apparent, as countries and hence industries will be committed to net-zero emissions by 2050.

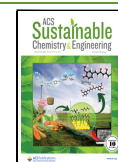
The decarbonization of cement manufacturing is currently challenging because the available CO<sub>2</sub> mitigation strategies are limited by the lack of economic incentives. Further policy efforts will be needed in the coming years. Potential strategies

have been proposed to curb carbon emissions in this hard-to-abate sector. These include (i) improving the energy efficiency of the cement process; (ii) switching to lower carbon fuels; (iii) promoting material efficiency (reducing the clinker-to-cement ratio); and (iv) implementing carbon capture and utilization and/or sequestration (CCUS) technologies. Some strategies as the improvement of energy efficiency are already being implemented, while others, such as those related to the emission reduction potential from using alternative fuels and clinker substitution, are expected in the short to midterm. On the contrary, the deployment of most of the emerging CCUS technologies at an industrial scale may take more than 20

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years. Despite this fact, CCUS implementation in cement manufacturing will be mandatory, as it can contribute to effectively curbing the releases of CO<sub>2</sub> from the calcination stage. Indeed, according to the cement decarbonization roadmap proposed by the International Energy Agency (IEA), CCUS could represent around 48% of CO<sub>2</sub> emission reduction by 2050.<sup>2</sup> Some technological challenges should be overcome for massive CO<sub>2</sub> recycling into value-added chemical products guaranteeing to be practical, realistic, and achievable from both economic and environmental perspectives.

A recent environmental study found in the literature has suggested a prospective decarbonization scenario for cement manufacturing with complete elimination of CO<sub>2</sub> emissions related to fossil fuel when a mix of 50% hydrogen (H<sub>2</sub>) and 50% biomass is used in the kiln and 83.3% biomass with 16.7% plasma is used in the calciner.<sup>3</sup> The authors assumed that using a proper combination of fuel switching and CO<sub>2</sub> capture from the process emissions, a net-zero-emission cement kiln could be envisaged. However, both fuel switching and CCUS still require innovative technologies to be implemented. Now, the efforts are focused on scaling up these CO<sub>2</sub> recycling technologies as soon as possible to make the decarbonization venture worthwhile within this hard-to-abate sector.

Today, CO<sub>2</sub> capture in the cement sector is close to commercial demonstration, with the world's largest CO<sub>2</sub> capture from cement kiln off-gas found at the pilot scale in Anhui Conch's Baimashan plant (China).<sup>4</sup> This plant is based on the mature amine absorption technology with a CO<sub>2</sub> capture capacity of 50,000 ton·y<sup>-1</sup> that accounts for 3% of the total CO<sub>2</sub> emissions from the cement factory.<sup>5</sup> The demonstration of CO<sub>2</sub> capture at a large scale is expected through a new capture plant based on amine chemical absorption in the Norcem cement plant (Brevik, Norway). It is expected to capture 50% of the factory's emissions using surpluses of waste heat. The captured CO<sub>2</sub> will be liquefied and stored under the North Sea.<sup>6</sup> Moreover, Dalmia Cement (India) has declared its intention to build a large-scale CCUS plant with a capacity of 0.5 Mt CO<sub>2</sub>·y<sup>-1</sup>, aiming to explore the possibilities to use the captured CO<sub>2</sub> for chemical manufacturing.<sup>7</sup> Second post-combustion capture generation, by membrane separation, has been recently proved at the pilot scale at the Brevik plant, showing stable performance and achieving 70% vol purity in a single stage.<sup>4</sup>

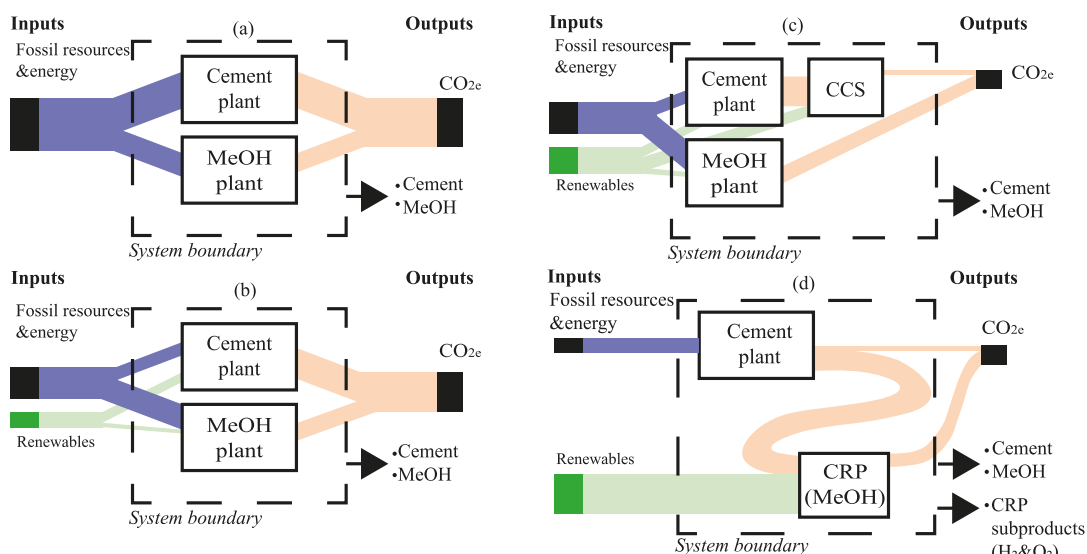
Despite that many CO<sub>2</sub> capture technologies are close to being commercialized, the environmental and economic feasibility of technologies for using the captured CO<sub>2</sub> remains unclear. Most of them are found at their infancy, with mineral carbonation to additives and hydrogenation of CO<sub>2</sub> to methanol close to the commercial scale.<sup>8,9</sup> To date, the preferred long-term decarbonization solution for cement factories is burying CO<sub>2</sub> underground by CCS, which is the most mature near-carbon-neutral technology. Its main challenges are the cost and energy penalty, followed by the location and capacity of storage sites.<sup>10</sup> In this sense, CO<sub>2</sub> recycling to produce value-added chemicals and fuels (by CCU) may complement CCS routes, offering additional benefits, especially when storage options are limited.<sup>8,11,12</sup> In this sense, CO<sub>2</sub> recycling benefits are beyond the CO<sub>2</sub> reduction potential, as it may result in synergic defossilization of CO<sub>2</sub>-based chemicals as the fossil resource consumption from their conventional processes is avoided.<sup>13</sup> Without a doubt, CO<sub>2</sub> capture from key sources and recycling appears to be the silver lining in climate change clouds. However, it

should be considered that as most of these valuable CO<sub>2</sub>-based products would compete in markets out of the cement vision (e.g., methanol, formic acid, ethylene, etc.), further policy efforts and economic incentives will be required to promote co-marketing of CO<sub>2</sub>-based chemicals and decarbonized basic products (e.g., cement).

The emerging electrochemical reduction (ER) has been demonstrated at the lab scale to produce several chemicals including methanol (CH<sub>3</sub>OH), formate/formic acid (HCOO<sup>-</sup>/HCOOH), methane (CH<sub>4</sub>), ethylene (C<sub>2</sub>H<sub>4</sub>), carbon monoxide (CO), and acetone (C<sub>3</sub>H<sub>6</sub>O).<sup>14–17</sup> In order to boost its further development, the present study focuses on the ER production of methanol (MeOH), an important building block and fuel, found at low technological readiness levels (TRL 3–4). The future sustainable implementation of this conversion technology in hard-to-abate sectors, like cement, can contribute to closing the anthropogenic carbon cycle in combination with other potential strategies such as CCS, providing defossilization of traditional MeOH market.<sup>18,19</sup>

In the latest decades, several efforts have been made to enhance the stability of CO<sub>2</sub> ER performance through the improvement of the catalyst design that avoids its deactivation, the improvement of the electrode and membrane engineering, and some system-level modifications. However, ER scale-up is still hampered by the low production rates, low current densities, and Faraday efficiencies that may result in high-energy requirements by the product separation. Several techno-economic analyses (TEAs) have examined the feasibility of ER of CO<sub>2</sub> technology at the large scale,<sup>20–26</sup> and even the construction of some pilot plants has been recently announced.<sup>27</sup> In a previous study carried out by the authors, ER of CO<sub>2</sub> to MeOH has been compared with the mature pathway of direct hydrogenation,<sup>9,28,29</sup> which is found to be at TRL 8–9.<sup>11</sup> The study carried out by the authors found the figures of merits of those key performance parameters needed in a sustainable long-term ER implementation.<sup>25</sup> However, most of the available TEAs and LCAs are focused on the challenges that must be overcome in the ER technology instead of focusing on synergic solutions between decarbonization and defossilization for particular sectors. In general, some TEAs of CO<sub>2</sub> recycling assume that a concentrated CO<sub>2</sub> flow is simply available,<sup>28,30–33</sup> while the vast majority assume that CO<sub>2</sub> comes from power plant flue gas.<sup>22,34–39</sup>

In the present study, a prospective ex-ante feasibility analysis through life cycle thinking has been conducted to demonstrate the synergic decarbonization and defossilization possibilities by the implementation of a carbon recycling plant (CRP) based on ER in a cement plant to co-produce CO<sub>2</sub>-based MeOH from the cement direct CO<sub>2</sub> emissions. The decarbonization potential of CRPs has been previously demonstrated by the authors in the hard-to-abate soda ash sector.<sup>40</sup> A reduction of soda ash carbon footprint (CF) of around 75% was found by the implementation of carbon capture and ER of CO<sub>2</sub> into MeOH. To the best of our knowledge, this is the first study that focuses on the benefits of the proposed CRP in the cement figures from the environmental perspective. This study will display the perspectives of carbon recycling scenarios that are expected in the next decades.



**Figure 1.** System boundary of scenarios: (a) Baseline (conventional); (b) Baseline-RWs; (c) Baseline-CCS; and (d) S-CRP.

## METHODOLOGY

**Goal and Scope.** The goal of the present study is to explore the carbon reduction and defossilization possibilities of CO<sub>2</sub> recycling management based on the emerging ER technology in the frame of long-term net-zero carbon cement production. This study evaluates the impact caused in both the greenhouse gas emissions and resource depletion by the synergic co-production of cement and methanol (MeOH), which is synthesized by ER technology from direct CO<sub>2</sub> emissions. Conventional cement and MeOH manufacturing from the ecoinvent database v3.7<sup>41</sup> will be used as the benchmark.

**Functional Unit and System Boundary.** The production capacity of the considered cement plant, used as the CO<sub>2</sub> source, is 1 Mton/y, which fits that of a traditional cement plant. The direct CO<sub>2</sub> emissions from cement manufacturing were considered to be 672 kg of CO<sub>2</sub>/ton of cement.<sup>42</sup> Then, an amount of 672 kton of CO<sub>2</sub>/y is available to be captured. The functional unit (FU) is the combined amount of 1 ton of cement + 429 kg of MeOH. Two main scenarios will be evaluated in this paper: (i) the conventional productions of cement and MeOH and (ii) the long-term decarbonization pathway, labeled as S-CRP. S-CRP considers the integration of a CRP in the cement plant that captures CO<sub>2</sub> and converts it into MeOH. The conventional cement and MeOH production, labeled as Baseline, will be used as the benchmark. In addition, we have included a Baseline subscenario where heat and electricity consumptions come from renewables (RWs) (e.g., green hydrogen and photovoltaics (PV solar)). This is labeled as Baseline-RWs, as the nearest decarbonization pathway. Note that other resources such as limestone, gypsum, metals, and natural gas, which are used as raw materials, cannot be substituted in Baseline-RWs, with only heat and electricity assumed as renewables. This may represent the prospective figures for the short-to-midterm decarbonization scenario. The CCS strategy will also be included as a third subscenario of the Baseline-RWs. The CCS strategy considers the capture of CO<sub>2</sub> and the compression and its sequestration, but the production of 429 kg of MeOH will be kept as in the Baseline. As was previously mentioned, the CCS strategy is currently the preferred mid-to-long-term carbon management for cement

manufacturing. Authors will display Baseline-CCS in the result section only as a benchmark. Note that the prospective exploration of CCS or a combination of CCUS is out of the scope of the present study because of the low TRL of the ER technology. The system boundaries of Baseline subscenarios and S-CRP are shown in Figure 1.

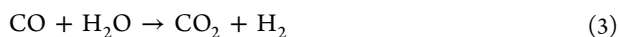
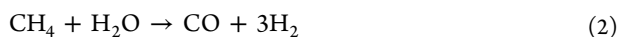
It should be noted that the technical analysis of this study must be read as preliminary as mass and energy balance was based on a mathematical model built by the authors. A detailed process simulation including the corresponding mass flows, compositions, and P&T in the involved streams is out of the scope of the present study. The novelty of this study is the evaluation of the decarbonization possibilities through CRP implementation to achieve low-carbon cement and defossilized MeOH productions. The utilization of MeOH is out of the system boundary, as we assumed that part of the fossil MeOH can be replaced in the market, and also, the utilization does not provide any valuable information in this study. The description of the scenarios and the inventories with input and output amounts is given in the following section.

**Scenarios and Life Cycle Inventories.** *Benchmark Scenario: Baseline, Baseline-RWs, and Baseline-CCS.* The Baseline scenario considered the integrated production of 1 ton of cement + 429 kg of MeOH by conventional production. Briefly, the conventional production of cement involves a calcination step that consists of the decomposition of limestone (CaCO<sub>3</sub>) at 900 °C to calcium oxide (CaO) and gaseous carbon dioxide (CO<sub>2</sub>), which is generated from process reaction 1. This step is followed by the clinkering process in which CaO reacts at a high temperature (typically 1400–1500 °C) with silica, alumina, and ferrous oxide to form silicates, aluminates, and ferrites of calcium, respectively, which produce the clinker. The clinker is then ground or milled together with gypsum and other additives to produce cement. Typically, 30–40% of direct CO<sub>2</sub> emissions come from the combustion of fuels, and the remaining (60–70%) come from the chemical reactions involved in converting CaCO<sub>3</sub> to CaO.<sup>2</sup>

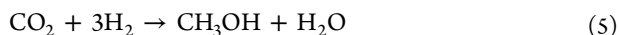


The conventional synthesis of MeOH is through steam reforming, which is performed in one or two steps in a tubular

reactor at 850–900 °C to leave as low methane as possible in the synthesis gas. The reaction of the steam reforming route can be formulated for methane, the major constituent of natural gas according to reactions 2 2–345, as follows



Methanol synthesis



Life cycle inventories from conventional cement production and methanol through steam reforming have been taken from the ecoinvent database v3.7<sup>41</sup> (Table 1).

**Table 1. Inventory of the Baseline Scenario for the FU**

	Baseline		unit
	cement	methanol	
	Inputs		
main raw materials <sup>a</sup>			
limestone	809		kg
calcareous marl	421		
natural gas	0.158	280	m <sup>3</sup>
gypsum	50		kg
clay	299		kg
heavy fuel oil	23		kg
petcoke	3.53		kg
hard coal	32		kg
water	307	365	kg
aluminum oxide		100	mg
copper oxide		40	mg
nickel		8.6	mg
molybdenum		4.29	mg
energy			
heat	3.8 <sup>b</sup>	2.8 <sup>c</sup>	GJ
electricity	90	32	kW h
	Outputs		
CO <sub>2</sub> direct	672		kg
cement	1.0		ton
MeOH		0.429	ton

<sup>a</sup>Only main raw materials are displayed. <sup>b</sup>Heat comes from hard coal, petcoke, and heavy fuel oil. <sup>c</sup>Heat comes from steam (natural gas).

In the Baseline-RW scenario, electricity is assumed to come from renewables (PV solar). Heat consumption to produce 1 ton of cement (3.8 GJ) was assumed to be supplied by 100% green H<sub>2</sub>. It must be taken into account that the technical and economic viability of the fuel switching (e.g., coal, petcoke, etc.) to 100% green H<sub>2</sub> and the required refurbishment of the cement plant are out of the scope of the present study. Authors have analyzed this scenario to obtain a possible timeline of environmental figures for the cement and MeOH productions within the next decades. The objective of the Baseline-RW scenario is to analyze the window of opportunity of fuel switching and CO<sub>2</sub> recycling strategies. Authors have carried out a cradle-to-gate calculation, including the upstream green H<sub>2</sub> production. Green H<sub>2</sub> production is proposed to be synthesized by the polymer electrolyte membrane (PEM) technology, which is currently at the commercial stage. Currently, PEM efficiency can range between 83 and 50 kW

h/kgH<sub>2</sub>.<sup>43</sup> In this study, the optimistic value of 50 kW h/kgH<sub>2</sub> is assumed as PEM energy efficiency. The lower calorific value of H<sub>2</sub> is used to calculate the H<sub>2</sub> requirement (~120 MJ/kg). Consumption of deionized water at 18 kg/kgH<sub>2</sub> is required by the PEM technology.<sup>44</sup> Regarding the heat consumption to produce 429 kg of MeOH (2.8 GJ), it is proposed to be renewable heat from an industrial electric boiler that is operated using renewables (PV solar). Electric boiler efficiency is ~99% according to the literature.<sup>45</sup> Electricity consumption to produce 1 ton of cement (90 kW h) and 429 kg of MeOH (32 kW h) is assumed to come from renewables (PV solar). Baseline-CCS includes the capture of CO<sub>2</sub> direct emissions from the cement plant. The capture module consists of the mature process based on the monoethanolamine (MEA) absorption with 90% efficiency. According to the literature, a make-up quantity of 5 g of MEA per kg of CO<sub>2</sub> enters the unit.<sup>46</sup> CO<sub>2</sub> compression, transport, and sequestration were modeled according to the literature.<sup>47</sup> The energy consumption of compression and injection steps is 117 kW h/t of CO<sub>2</sub>.<sup>47</sup> It has to be remarked that both Baseline-RW and Baseline-CCS subscenarios are basic approaches and they were used only as a reference. Their prospective assessment including the exhaustive analysis and simulation of CCS and the analysis of the influences of the CO<sub>2</sub> transport stage and CO<sub>2</sub> leakage through the pipeline is out of the scope of the present study, and they were not considered.

**Long-Term Decarbonized Scenario: S-CRP.** The proposed S-CRP scenario in this study considers that the amount of MeOH is produced through the recycled CO<sub>2</sub> direct emissions released from the cement plant. Hence, the consumption of fossil resources from the MeOH conventional process is avoided that is mainly natural gas (280 m<sup>3</sup>/FU). The CRP scheme was based on the latest technological developments: (i) CO<sub>2</sub> capture unit by chemical absorption using MEA with 90% efficiency<sup>46</sup> and (ii) the production of MeOH by the ER of CO<sub>2</sub>.<sup>25</sup> The capture technology based on absorption using MEA was chosen, as it is a well-established end-of-pipe technology. A make-up quantity of 5 g of MEA is required per kg of CO<sub>2</sub> that enters the unit. The MEA process requires a substantial amount of heat for solvent regeneration, while power supply is required for operating fans and pumps and for compression and dehydration of the CO<sub>2</sub> that is captured. Energy consumptions of 3.90 GJ and 109 kW h/kg of CO<sub>2</sub> captured are required according to the literature.<sup>46,48</sup> In S-CRP, electric renewable heat is assumed for the capture step and the distillation. For this purpose, an electric boiler powered with PV solar with 99% heat/electricity efficiency is considered for heat supply.<sup>49</sup> The CO<sub>2</sub> conversion involves three main steps: (i) the ER of CO<sub>2</sub> based on a stack of individual cells; (ii) the distillation of the MeOH/water mixture up to the desired purity (99.7% wt); and (iii) the compression of the subproducts (H<sub>2</sub> and O<sub>2</sub>). H<sub>2</sub> is produced in a parallel reaction in the cathode compartment, while O<sub>2</sub> is produced in the anode by the oxygen evolution reaction (OER). The study considers both subproducts as a credit, which are accounted as avoided emissions and resource consumption from their conventional processes. The energy needed to transform H<sub>2</sub> and O<sub>2</sub> into the liquid forms to be ready to transport is accounted by the mathematical model. The consumption values by the distillation and compression steps are shown in the [Supporting Information](#). The CRP is powered by photovoltaics (PV solar) for the reduction step and heat as electric steam (from an electric boiler unit) for the

separation step according to the nature of each single process. MeOH is supposed to be synthesized in the ER stack. As the technology of ER of CO<sub>2</sub> into MeOH is found at the demonstration stage in the lab scale (TRL < 4), three timeline subscenarios of S-CRP will be assessed: (i) *status quo*; (ii) 2030; and (iii) 2050. Subscenario CRP-*status quo* is the current situation, while a certain degree of progress in ER parameters has been considered in S-CRP-2030 and S-CRP-2050 (Table 2) according to the recommended methodology for a prospective life cycle assessment.<sup>50</sup>

**Table 2. Current and Prospective ER Performance in the S-CRP Subscenarios**

parameter/subscenario	<i>status quo</i>	2030	2050
faradaic efficiency (%)	77.6	80	90
current density (mA·cm <sup>-2</sup> )	41.5	200	300
overall cell voltage (V)	2.67	2.3	2
single-pass CO <sub>2</sub> conversion [MeOH] (% wt)	<0.1	20	40

The subscenario *status quo* represents the recent progress on ER of CO<sub>2</sub> to MeOH. Yang et al.<sup>51</sup> has reported an outstanding performance for ER of CO<sub>2</sub> to MeOH using copper selenide nanocatalysts with a Faradaic efficiency of 77.6%, at a current density of 41.5 mA·cm<sup>-2</sup> and at a low overpotential of 285 mV. A certain degree of progress in ER parameters has been considered in the subscenarios 2030 and 2050. An ER cell total current of 200 mA/cm<sup>2</sup>, ER cell voltage of 2.3 V, and Faraday efficiency of 80% have been fixed for the near-term 2030 scenario based on ER performances for other reduction products demonstrated at the lab scale.<sup>52</sup> For the long-term 2050 scenario, the current density is fixed at 300 mA/cm<sup>2</sup> under an EC cell voltage of 2 V following the performance of commercial alkaline electrolyzers.<sup>22,53</sup> Faradaic efficiencies of 90% have already been reported at the lab scale for several ER products such as methane,<sup>54,55</sup> carbon monoxide,<sup>56,57</sup> and formic acid.<sup>58–61</sup> Regarding CO<sub>2</sub> conversion, it is not often reported in the literature. A conversion of 35% was selected for the *status quo* subscenario according to a recent lab-scale study.<sup>51</sup> Regarding 2030 and 2050 subscenarios, a reactor conversion of 50% was chosen for both cases as an expected better electrolyzer design could potentially boost the CO<sub>2</sub> conversion.<sup>22</sup> The S-CRP 2030 scenario assumes a MeOH concentration of 20% wt at the outlet of the ER cell that was set according to the current concentrations for formic acid (TRL 6), whereas the 2050 scenario assumes 40% wt MeOH. MeOH concentration in the 2050 scenario was set according to the long-term figures of merits found by the authors in a previous study.<sup>25</sup>

A detailed description of the mathematical model that describes the ER of CO<sub>2</sub> and the separation steps was built based on mass and energy balances and can be found in our previous study.<sup>25</sup> The details of the mathematical model that describes the CO<sub>2</sub> capture, ER, and distillation can be found in the Supporting Information. The detailed inventory of S-CRP is summarized in Table 3.

**Life Cycle Assessment.** An ex-ante life cycle assessment (LCA) will be used in the decision making to evaluate the best environmental performance and to compare the analyzed scenarios in terms of CF and resource depletion. Ex-ante LCA is commonly used as an early-on support tool to understand the implications of design choices on the anticipated

**Table 3. Inventory of the S-CRP Scenario (Per FU)**

inputs	value	unit
Main Raw Materials for the Cement Plant <sup>a</sup>		
limestone	809	kg
calcareous marl	421	kg
natural gas	0.158	m <sup>3</sup>
gypsum	50	kg
clay	299	kg
heavy fuel oil	23	kg
petcoke	3.53	kg
hard coal	32	kg
water	307	kg
Main Raw Materials for the CRP		
CO <sub>2</sub> (captured)	606	kg
water	365	kg
energy		
heat	3.8	GJ
electricity cement	0.090	MW h
electricity capture <sup>b</sup>	0.57	MW h
electricity ER	variable <sup>c</sup>	MW h
electricity purification	variable <sup>d</sup>	MW h
Products		
CO <sub>2</sub> direct emissions	66	kg
cement	1.0	ton
MeOH	429	kg

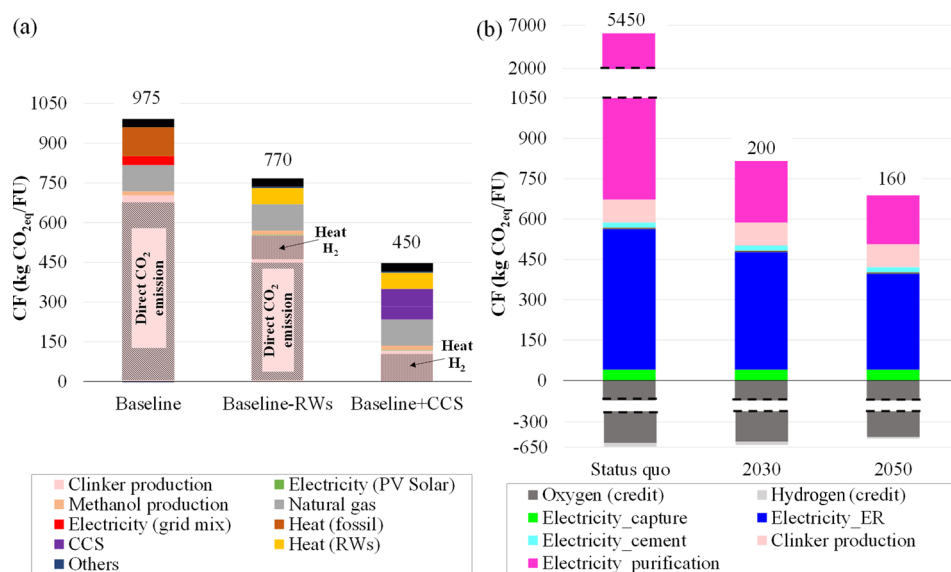
<sup>a</sup>Only the main raw materials for the cement main plant are displayed.

<sup>b</sup>Electricity is needed produce heat to supply the reboiler. <sup>c</sup>The consumption values for ER are 7.4 MW h (*status quo*), 6.2 MW h (2030), and 4.7 MW h (2050). <sup>d</sup>The consumption values for distillation are 79.8 MW h (*status quo*), 3.3 MW h (2030), and 2.6 MW h (2050).

environmental performance of the proposed CO<sub>2</sub> recycling technology.<sup>62</sup> The LCA framework followed in the present study involves four iterative phases: goal and scope definition, inventory analysis, impact assessment, and interpretation of results according to the international standard series ISO 14040:2006 and 14044:2006.<sup>63,64</sup> LCA software GaBi version 9.2 (Sphera)<sup>65</sup> was used to evaluate the environmental impact. An attributional process-based approach is applied, which accounts for relevant physical flows (i.e., resources, material, energy, and emissions) attributed to the provision of a specified amount of the FU across the lifecycle. The ReCiPe method was used with a hierarchic perspective. The approach considered was cradle-to-gate with the transport, use, and the end of life excluded from the present study. Global warming potential (GWP<sub>100</sub>) was the impact category selected as the metric of the CF. Fossil depletion (FD) was the metric for resource depletion since the CRP involves not only CO<sub>2</sub> emission reduction but also fossil resource saving.<sup>28</sup> FD measures the depletion of fossil fuels, that is, natural gas, oil, and coal. Environmental categories other than CF and FD were excluded from this study because the viability of the suggested strategy should be first fulfilled for the category intended to benefit from the CO<sub>2</sub> recycling implementation.

## RESULTS AND DISCUSSION

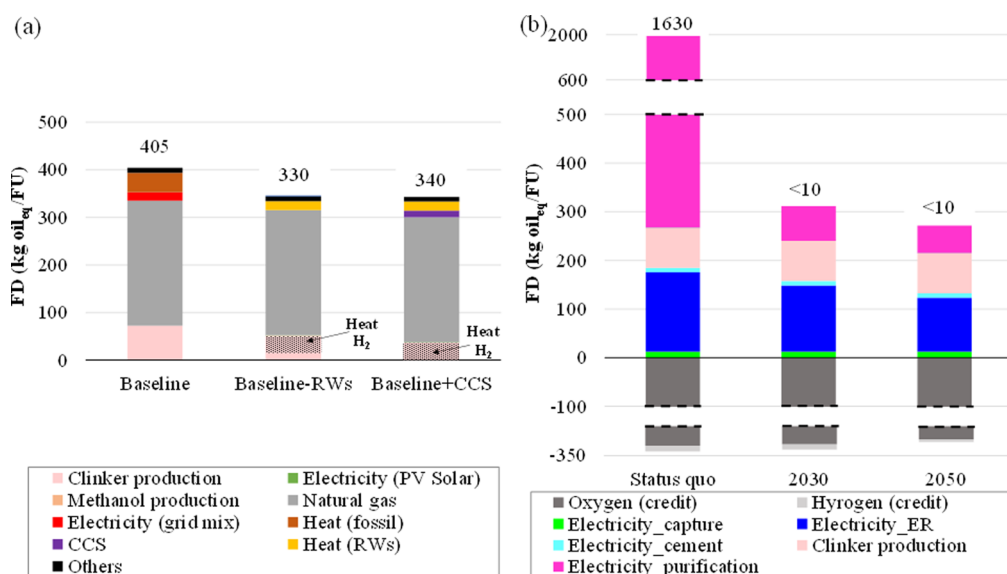
**Carbon Footprint and Fossil Resource Depletion Assessments.** Figure 2 displays the breakdown results of CF in the studied scenarios for joint cement and MeOH production (1 ton of cement and 429 kg of MeOH as the FU). An overall CF value of 975 kg CO<sub>2eq</sub>/FU was obtained for the



**Figure 2.** Breakdown of CF results for (a) Baseline, Baseline-RWs, and Baseline-CCS and (b) S-CRP subscenarios.

Baseline scenario (Figure 2a) that is used as a reference. It can be observed that the main influence in the Baseline overall CF value is the clinker production that represents a contribution of 720 kg CO<sub>2eq</sub>/FU, 85% of this value being direct CO<sub>2</sub> emissions according to its dataset.<sup>41</sup> As was mentioned before, fuel combustion is responsible for 30% of cement direct CO<sub>2</sub> emissions and the calcination of limestone is responsible for the remainder. In this sense, the fuel combustion switching strategy, which is the nearest-term decarbonization pathway, could reduce the overall CF value up to around 790 kg CO<sub>2eq</sub>/FU if no renewable impact would be considered. A recent fuel switching study found in the literature has assumed a complete elimination of direct CO<sub>2</sub> emissions related to fossil fuel in cement manufacturing using a mixture of 50% hydrogen (H<sub>2</sub>) and 50% biomass in the kiln and using 83.3% biomass with 16.7% plasma in the calciner using a plasma burner.<sup>3</sup> That study highlights that fuel switching requires refurbishment, the estimated total cost of the clinker being around 21.74 €/ton<sub>clinker</sub>.<sup>3</sup> Briefly, this strategy would require a new hydrogen burner, a storage tank, the renovation of pipelines, and a plasma torch system. Plasma torch system costs are in the range of 5–10 M€ according to the mentioned study. However, the authors of that study used a cradle-to-cradle approach, and then, no green H<sub>2</sub> production, plasma torch, and other impacts were included. In the present study, we have analyzed the possible influence of 100% heat supply using green H<sub>2</sub>. This intermediate scenario can be used here as the reference for the fuel switching strategy. As it can be observed in the right-side bar of Figure 2a, direct CO<sub>2</sub> emissions from 1 ton of cement production can be reduced up to 434 kg CO<sub>2eq</sub> but the production of green H<sub>2</sub> to power the kiln involves a contribution to the overall CF of around 105 kg CO<sub>2eq</sub>/FU that may shadow the overall benefits. Under the considered assumptions, the fuel switching strategy could reduce the CF from 975 up to 770 kg CO<sub>2eq</sub>/FU when the influence of green H<sub>2</sub> production and RW electricity is considered. This indicates that the decarbonization window achieved by the fuel switching strategy is around 20%. A positive trade-off between the impact of green H<sub>2</sub> production (and the RW electricity) and the effective CO<sub>2</sub> direct emission reduction in cement production should be further explored in this field. Baseline-

CCS could reduce the CF by more than 50% (450 kg CO<sub>2eq</sub>/FU) when green H<sub>2</sub> and PV solar electricity are used to power the heat and electricity requirements of the cement plant, respectively. Figure 2b displays the results of the CF when CO<sub>2</sub> recycling through CRPs is selected as the decarbonization strategy for the cement sector. The main benefit is the possibility to transform the vast majority of direct CO<sub>2</sub> into a value-added product (as MeOH), and then, it contributes to synergic decarbonization of cement production and defossilization of MeOH markets. Notice that no fuel switching strategy was included in the S-CRP subscenarios to avoid the introduction of additional uncertainties because both strategies are not currently commercial and no data are available. The performance of the cement plant in S-CRP was the same as in the Baseline scenario; only CO<sub>2</sub> direct emissions are removed from the cement plant and fed to the capture unit in the CRP to demonstrate the potential of S-CRP in comparison to the fuel switching strategy. The CF value of the S-CRP subscenario *status quo* is notably higher than that of the Baseline (5450 kg CO<sub>2eq</sub>/FU) because of the current excessive electricity requirements by the purification stage. This fact was expected due to the present low production rate of MeOH, which is synthesized in the ER cell at 0.1% wt. This low concentration involves excessive electricity consumption by the electric boiler (79.8 MW h/FU) to power the separation stage (distillation). The CF values of S-CRP 2030 and 2050 were 200 and 160 kg CO<sub>2eq</sub>/FU, respectively. As it can be observed, these values represent a sharp reduction compared with the conventional production (Baseline). Specifically, this reduction is found in the range of 75–80%. As it was mentioned in the methodology section, the S-CRP 2030 scenario assumes a MeOH concentration of 20% wt at the outlet of the ER cell. The concentration was set according to the current concentrations for formic acid, found at a higher TRL (TRL 6).<sup>11</sup> On the other hand, the 2050 subscenario assumes a MeOH concentration at the outlet stream of the ER cell of 40% wt, which is in agreement with the long-term figures of merits found by the authors in a previous study.<sup>25</sup> The main contributor to the CF in subscenarios S-CRP 2030 and 2050 is the electricity consumption to power the ER cell followed by the electricity consumption by the distillation. The ER cell

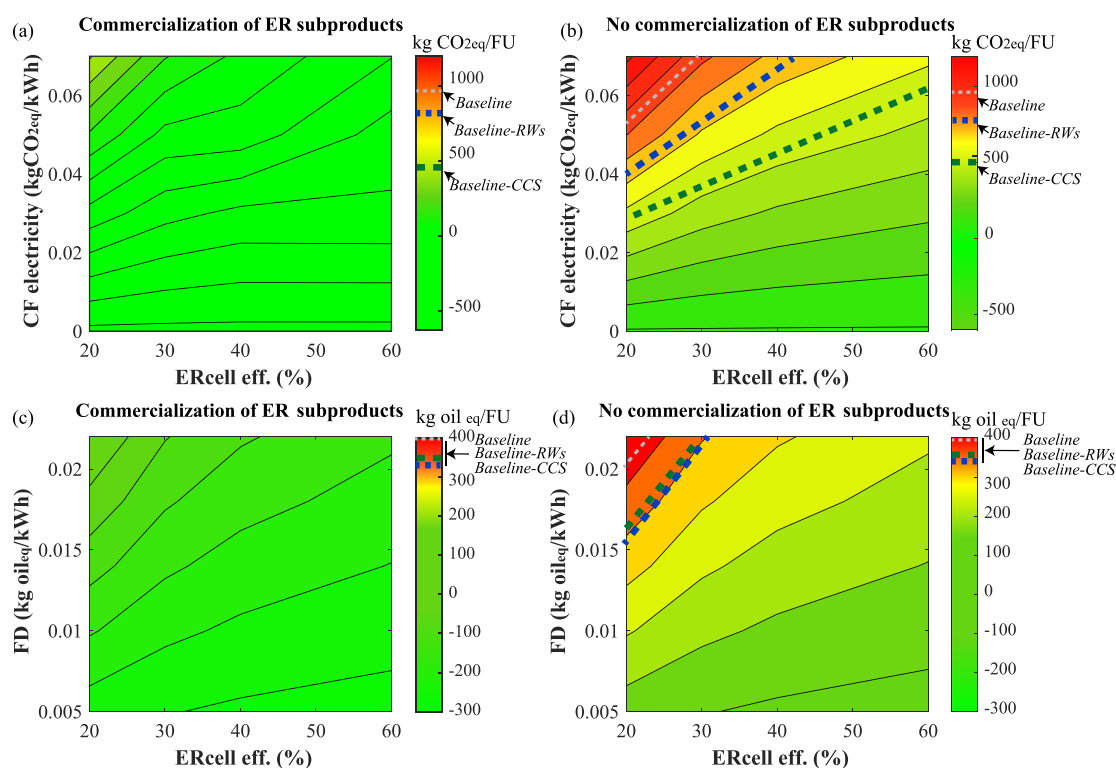


**Figure 3.** Breakdown of FD results for (a) Baseline, Baseline-RWs, and Baseline-CCS and (b) S-CRP subscenarios.

subproducts H<sub>2</sub> (from the cathode parasitic reaction) and O<sub>2</sub> (produced in the anode) have been pondered over as credits for the CF. This result highlights the necessity of low-carbon electricity for a sustainable CRP implementation. These results have been obtained using the current CF of PV solar electricity (0.067 kg CO<sub>2eq</sub>/kW h), but the expected improvement of renewable energy systems in the coming years should be highlighted. For example, recent advances have led to PV modules with higher efficiencies and lifespans.<sup>66</sup> The influence of the CF of PV solar and the energy efficiency of the conversion process technology will be evaluated through a sensitivity assessment in the following section. It should be mentioned that the complete commercialization of the mentioned subproducts is optimistic, especially in the case of anodic O<sub>2</sub>, which has a low commercial value. Nonetheless, alternative anodes to OER are currently being explored, such as the glycerol electro-oxidation (GEO) anode. Anodes based on the GEO reaction may not reduce the energy consumption of the ER cell but can produce more valuable anodic products than O<sub>2</sub>.<sup>67,68</sup>

The resource depletion assessment has been carried out using the environmental category FD (shown in kg oil<sub>eq</sub>/FU). Figure 3 shows the breakdown results of the analyzed scenarios and the FU (1 ton of cement and 429 kg MeOH). The FD overall value of the Baseline scenario was found around 405 kg oil<sub>eq</sub> per FU, the main contributor to this value being the natural gas, which is used as a raw material to produce MeOH. As it can be observed in Figure 3a, the benefits in Baseline-RWs and Baseline-CCS are scarce and FD decreases to 330 kg oil<sub>eq</sub> per FU and 340 kg oil<sub>eq</sub> per FU, respectively. In particular, natural gas involves a contribution of 263 kg oil<sub>eq</sub> to the overall FD values in these scenarios. The second-largest contributor to FD is the clinker production, with a contribution of 83 kg oil<sub>eq</sub> per FU in the Baseline scenario, which decreases to 36.5 kg oil<sub>eq</sub> per FU and 4.0 kg oil<sub>eq</sub> per FU in Baseline-RWs and Baseline-CCS, respectively. Specifically, the clinker production process uses hard coal and heavy fuel oil, among others, in the kiln. Hard coal and heavy fuel oil contribute to the FD overall value of 27.4 and 27.9 kg oil<sub>eq</sub>, respectively (66% to the clinker FD share). The third contributor to the overall FD value of the Baseline is the fossil heat consumption, which represents a

value of 41 kg oil<sub>eq</sub> per FU (2.8 GJ is used to produce 429 kg of MeOH). Note that Baseline-RWs and Baseline-CCS substitute fossil fuels and heat with green H<sub>2</sub>. In addition, in the scenario Baseline-CCS, direct CO<sub>2</sub> emissions are captured. A positive trade-off was found between the FD caused by the renewable PV solar consumption that is used to produce green H<sub>2</sub> and to capture and sequester CO<sub>2</sub> direct emissions and the FD of fossil fuels that are saved in this scenario. As it can be observed in Figure 3b, the production of MeOH by CO<sub>2</sub> in S-CRP entails a considerable reduction of fossil resource consumption. The amount of natural gas used in conventional MeOH production (280 m<sup>3</sup>) and the industrial heat from natural gas (2.8 GJ) are completely saved in the three S-CRP subscenarios. On the contrary, the high renewable electricity consumption by the S-CRP should be remarked because the capture, conversion, and purification processes are fully electrified. A positive trade-off between resource savings and renewable consumption must be found. It is well known that photovoltaic (PV) modules, for example, crystalline silicon (c-Si) wafer, involve consumption of resources during the production, and then, the FD category must also be evaluated in S-CRP.<sup>69</sup> As displayed in Figure 3b, the main contributor to FD in the studied subscenarios is the PV solar electricity required to power the distillation stage, followed by the PV solar electricity needed to power the ER cell unit. A positive trade-off between the fossil resource savings by the S-CRP and the resources needed to produce PV solar electricity has been achieved in both 2030 and 2050 S-CRP subscenarios. The overall FD values of both scenarios are close to 300 kg oil<sub>eq</sub> per FU, which is below the Baseline FD value (405 kg oil<sub>eq</sub> per FU). Current efforts on the development of renewable electricity technology are now focused on the production of more sustainable collector systems with a higher lifespan and of course in recycling processes to recover the materials from the current turbines and PV modules.<sup>66</sup> In this context, lower FD of PV solar electricity is expected in the coming years. Additionally, when the commercialization of subproducts H<sub>2</sub> (from the cathode parasitic reaction) and O<sub>2</sub> (produced in the anode) is considered, they are pondered over as credits for the FD value in S-CRP (represented in gray color). The resource consumption by their conventional productions is avoided,



**Figure 4.** Sensitivity assessment of the influence of prospective CF and FD of PV solar electricity and the energy efficiency of the ER cell in the impact categories CF (a,b) and FD (c,d) with and without the commercialization of  $H_2$  and  $O_2$  subproducts.

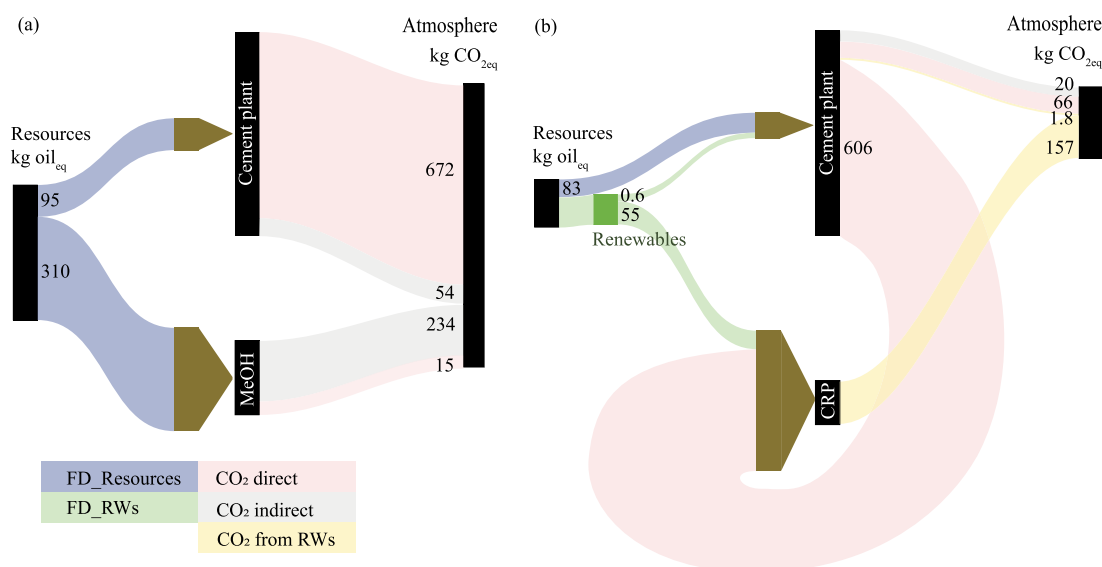
which consists of steam methane reforming (for  $H_2$ ) and cryogenic air separation (for  $O_2$ ). The FD overall value sharply decreases below 10 kg oil<sub>eq</sub>/FU. Note that the complete commercialization of the mentioned subproducts is optimistic, especially in the case of anodic  $O_2$ , which has a low market value. However, the obtained value under the assumption of full commercialization (<10 kg oil<sub>eq</sub>/FU) shows the complete window of opportunity for S-CRP.

**Sensitivity Analysis.** The previous environmental results have demonstrated that the ER cell electricity consumption and the purification stages are the main constraints to achieving a sustainable ER scale-up and a final CRP implementation in hard-to-abate sector sustainable implementation. This is in agreement with previous environmental studies.<sup>30,70–72</sup> This fact reveals the importance of the availability of low-impact electricity in both the CF and FD categories. RWs such as PV solar (considered in this study) or others such as wind electricity should be used to power CRPs, ensuring a sustainable implementation. In the previous section, we have conducted LCA fixing the PV solar impacts at current impact values of CF (0.07 kg CO<sub>2eq</sub>/kWh) and FD (0.02 kg oil<sub>eq</sub>/kWh) according to the Spanish PV solar average.<sup>41</sup> Figure 4 displays the results of a sensitivity assessment of the long-term S-CRP 2050 subscenario. The influence of the ER cell energy efficiency and the CF and FD of the electricity source in the CF and FD of the FU is shown, which is the integrated amount of MeOH and cement. Considerable influence can also be observed when the commercialization of subproducts ( $H_2$  and  $O_2$ ) is included (Figure 4a–c) or when they are neglected and assumed as a discharge to the atmosphere (Figure 4b–d). The obtained results indicate that the commercialization of other ER subproducts may represent a clear benefit for the FD category, as they are avoided from

their fossil markets and then considered as credit. We consider that the assumption of full commercialization of subproducts is too optimistic, especially for  $O_2$ , which has a low market value. The authors consider that a real situation will be near the results displayed in Figure 4b–d, which means that  $H_2$  and  $O_2$  are neglected. ER cell efficiencies should be above 35% to achieve a sustainable scenario if the electricity source impact values are found around the current PV solar. Note that values near the Baseline CF (975 kg CO<sub>2eq</sub>/FU) and FD (405 kg oil<sub>eq</sub>/FU) are considered as the upper frame reference (shown in red color). The current ER cell efficiency for MeOH is found at 35% (in S-CRP *status quo*), but efficiencies over 60% have been considered in the long-term figures of merits for the CO<sub>2</sub> conversion into MeOH.<sup>73</sup> This long-term efficiency value is quite close to the corresponding value for the state-of-the-art technology of water splitting electrolysis, which is found at TRL 7–8.<sup>74</sup> Moderate ER cell efficiencies will require electricity sources with environmental impact below 0.02 kg CO<sub>2eq</sub>/kWh and 0.01 kg oil<sub>eq</sub>/kWh to be below the Baseline upper frame. These electricity impact values are close to the current wind electricity impacts, which are around 0.02 kg CO<sub>2eq</sub>/kWh (CF) and 0.006 kg oil<sub>eq</sub>/kWh (FD) according to the approach of wind onshore Spanish average.<sup>41</sup> The utilization of wind electricity would be a powerful alternative to PV solar, but it will depend on the specific place and the availability of these RW sources.

The obtained results hypothesized that long-term low-carbon cement and MeOH joint productions will require the availability of low-carbon electricity sources (<0.02 kg CO<sub>2eq</sub>/kWh) with a low-FD impact (<0.01 kg oil<sub>eq</sub>/kWh). We have analyzed the scenario S-CRP 2050 considering low-carbon electricity (0.02 kg CO<sub>2eq</sub>/kWh) with a low-FD impact (0.007 kg oil<sub>eq</sub>/kWh) that corresponds with the current impact values





**Figure 5.** FD and carbon emissions for the production of cement (1 ton) and MeOH (429 kg) in (a) Baseline and (b) long-term low-carbon S-CRP (cradle-to-gate approach).

of the Spanish wind electricity (onshore).<sup>41</sup> Figure 5 displays the CF and FD values in the Baseline scenario and the positive trade-off found by the low-carbon S-CRP 2050 approach. As it can be observed, in the S-CRP 2050 scenario, the penetration of this low carbon renewable electricity in both CRPs and cement plants has been included. Cement production requires only 90 kW h/FU, whereas the CRP needs 7.9 MW h/FU. These consumptions of electricity lead to impacts of 0.06 and 1.8 kg CO<sub>2eq</sub>/FU (cement plant) and 55 kg oil<sub>eq</sub>/FU and 157 kg CO<sub>2eq</sub>/FU (CRP). A positive trade-off between the resource savings (respect the baseline) and the renewable energy requirements by the S-CRP has been achieved. In particular, 310 kg oil<sub>eq</sub>/FU, mainly due to the natural gas needed in conventional MeOH production, is avoided and substituted by the utilization of 606 kg of recycled CO<sub>2</sub> from direct cement emissions. The requirement of renewable electricity to reduce the stable CO<sub>2</sub> molecule into MeOH entails a value of 55 kg oil<sub>eq</sub>/FU mainly because of wind turbine production. CF and FD may decrease from 975 kg CO<sub>2eq</sub>/FU and 405 kg oil<sub>eq</sub>/FU to 264 kg CO<sub>2eq</sub>/FU and 136 kg oil<sub>eq</sub>/FU, respectively. This decrement could be even more noticeable under the expected future sustainable developments for the renewable electricity market. Note that Figure 5b does not include the credits from the commercialization of any other ER subproducts such as O<sub>2</sub> and H<sub>2</sub>. Of course, these ER cell subproducts were commercialized, and the CF and FD might be even negative, providing the CRP strategy as a real GHG sink.

The development of CCU technologies, such as ER, is expected to play a key role in a future carbon-neutral economy, especially when combined with CCS and/or fuel switching strategies. This study is intended to show the potential benefits of carbon capture and recycling by ER into methanol (TRL < 4), boosting the innovation for its future deployment in hard-to-abate sectors such as cement production. This study has identified a possible trade-off between renewable consumption and resource savings in which ER may operate sustainably. However, it should be noted that certain assumptions and limitations affecting this study should be dealt with in further research. These assumptions include the following:

- The application of an ex-ante LCA in this study deals with limited data. Methanol production by ER of CO<sub>2</sub> currently has a low TRL (TRL<4), and a certain degree of progress in ER parameters has been considered (S-CRP-2030 and S-CRP-2050). These assumptions have been made according to the recommended methodology for a prospective LCA. Therefore, our results and findings should be considered as a particular case study, rather than the definitive evidence.
- The scenarios presented in this study are a simplification of a complex reality. Of course, complementary scenarios including a combination of different strategies including CCS and fuel switching are possible. Given the low TRL of the technology studied here, we conducted a prospective ex-ante LCA as a first approach. Consequential and/or dynamic LCAs are a crucial task to be carried out in the future in order to evaluate other physical and economic causalities related to the development and implementation of the current portfolio of decarbonization technologies and renewables penetration.

## CONCLUSIONS

This study has demonstrated the potential window of opportunity of the carbon recycling strategy in the cement sector in comparison with the fuel switching pathway. A sustainable fuel switching implementation would require finding a positive trade-off between renewable fuel production (e.g., green H<sub>2</sub> production and RW electricity) and the fossil fuel impacts. The full window of opportunity to reduce CO<sub>2</sub> direct emissions of the fuel switching strategy is around 30% that may be shadowed by the impact of the renewable heat and electricity. In this sense, carbon capture and utilization and/or sequestration (CCUS) is the preferred long-term strategy, as it can improve the full window of opportunity to reduce CO<sub>2</sub> up to 75%. This study is focused on the possibilities to reduce the CF and the FD when methanol (MeOH) is produced from the cement CO<sub>2</sub> direct emissions by a sustainable implementation of a CRP based on the emerging ER technology. Low MeOH production rate, which leads to high electricity consumption by

the purification step, is currently the main obstacle for scaling up ER conversion technology. However, a concentration of MeOH between 20 and 40% wt at the ER cell will ensure sustainable implementation of the CRP compared with the conventional productions. CF reduction between 75 and 80% with respect to the conventional cement and MeOH productions could be achieved under the expected ER technology development for 2030 and 2050. Considering the expected sustainability improvement in renewable electricity production systems and the progress of the ER technology, a positive trade-off between renewable consumption and resource savings has been demonstrated. Specifically, a long-term low-carbon cement and MeOH integrated production will require the availability of low-carbon electricity sources ( $<0.02$  kg CO<sub>2,eq</sub>/kW h) with a low-FD impact ( $<0.01$  kg oil<sub>eq</sub>/kW h). Under these conditions, the decarbonization strategy based on the CRP implementation may represent a step further regarding the fossil switching strategy, which is currently the preferred short-term decarbonization pathway. The insights gained in this study may be of assistance in the sustainable scale-up and implementation of ER in hard-to-abate sectors.

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acssuschemeng.1c06118>.

Model description of the S-CRP scenario, main and side electrochemical reactions, mass and energy balances, description of the distillation of the MeOH model, and list of hypotheses used in the mathematical model (PDF)

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### Author Contributions

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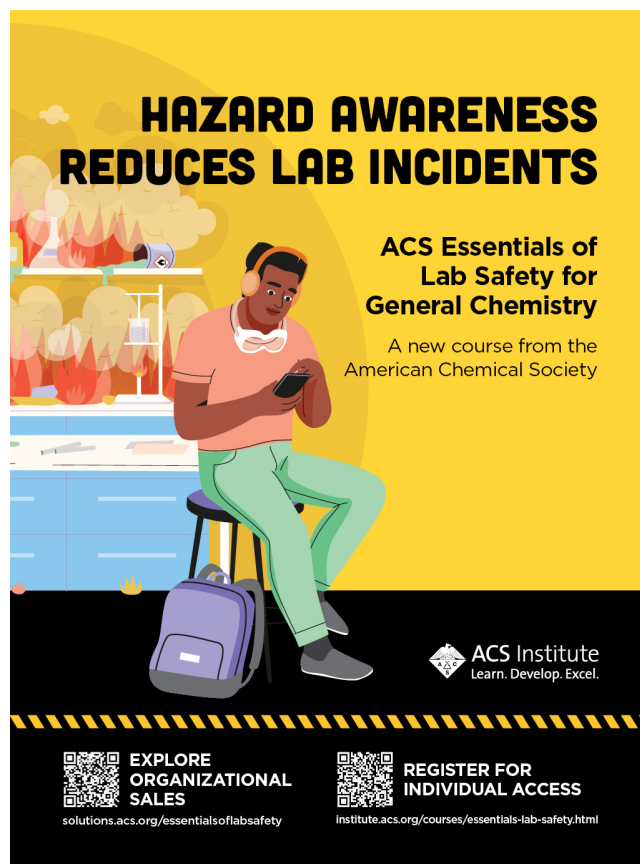
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