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## Decarbonising the lime industry: State-of-the-art

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### ABSTRACT

The thermal treatment of limestone (mainly  $\text{CaCO}_3$ ) to produce lime ( $\text{CaO}$ ) is a major contributor to  $\text{CO}_2$  emissions and the literature on decarbonising the lime industry is scarce. Subsequent hydration of lime would lead to the synthesis of slaked/hydrated lime  $\text{Ca(OH)}_2$ ; the production of a tonne of  $\text{Ca(OH)}_2$  emits  $\sim 1.2$  tonnes of  $\text{CO}_2$  arising mainly from the process chemistry and fossil fuel combustion. Carbon Capture & Storage (CCS) technologies are currently believed to have the highest potential to mitigate these  $\text{CO}_2$  emissions, assuming that the thermal calcination of  $\text{CaCO}_3$  is unavoidable. Despite intensive research efforts and development, CCS technologies cannot be industrially applied yet due to their limited efficiency and the associated capital and operational costs.

In this review, the current state of the lime industry and its processing configurations is visualised. This is followed by a detailed description of the current status of the relevant CCS technologies (including their  $\text{CO}_2$  avoidance costs) and eco-efficient alternative fuels. This work then gives voice to two novel and potentially more sustainable decarbonisation routes that do not involve the thermal calcination of  $\text{CaCO}_3$ , one of which involves simultaneous mineralisation leading to permanent storage of  $\text{CO}_2$ . These technologies are particularly interesting especially if high temperature lime kilns, as we know them, are phased out to meet climate goals. It is revealed that the energy shift to green electricity might lead to a no-carbon lime industry and subsequent carbon neutrality (or negativity) of other hard-to-abate sectors.

### 1. The slaked lime industry

The term “lime” is usually used to refer to all those products deriving from the calcination of limestone and/or chalk, although they may be classified as: quicklime  $\text{CaO}$ , hard-burnt lime  $\text{CaO}$ , slaked/hydrated lime  $\text{Ca(OH)}_2$ , and dolomitic lime (e.g., 30 wt%  $\text{CaO}$ , 21 wt%  $\text{MgO}$ , and 45 wt %  $\text{CO}_2$  in the original limestone [1]).  $\text{CaO}$ , the main product of the calcination of limestone, is the most in demand simple oxide worldwide, considering that it is also the primary precursor for the cement industry [2]. Depending on the average diameter size  $D$ , different quicklimes may be obtained: large lump lime ( $D < 20$  cm), pebble lime ( $0.6$  cm  $< D < 2.5$  cm), ground lime ( $D < 0.25$  cm), pulverised lime ( $D < 10^{-4}$  cm), and pelletised lime ( $D \approx 2.5$  cm). Quicklime reacts spontaneously with water, and its transport requires strict safety measures, given the strong exothermicity of its hydration reaction (1.14 MJ released per kg of  $\text{CaO}$  hydrated [3]). Outside the cement industry, a significant portion of  $\text{CaO}$  (around 27% in the EU in 2017 [4]) would be hydrated and stored as Ca

$(\text{OH})_2$ , finding application in a wide range of industries, such as: iron and steel manufacturing for the treatment of the acid effluents and heavy metals removal [5], construction [6], soil stabilisation [7], removal of contaminants (e.g. As, F) from potable water [8], low-temperature desulfurization [9] and sulfur scrubbing [10],  $\text{CO}_2$  capture [11], wastewater treatment [12], bulk chemicals [13], pharmaceuticals, and cosmetics. In 2020, out of the 70 Mt globally produced, the EU market accounted for the manufacturing of 17.4 and 4.8 Mt of  $\text{CaO}$  and  $\text{Ca(OH)}_2$ , respectively [4]. The ability and advanced technological understanding of using  $\text{CaO}/\text{Ca(OH)}_2$  to capture and store  $\text{CO}_2$  makes it useful for enabling net-zero emissions across several industries [14].

The slaked lime manufacturing process involves quarrying, crushing, washing, and stone preparation of the raw limestone prior to calcination into  $\text{CaO}$  (Equation (1)) and subsequent hydration to  $\text{Ca(OH)}_2$  (Equation (2)).



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Abbreviations			
Annular Shaft Kiln	ASK	Flue Gas Recycle	FGR
Air Separation Unit	ASU	Lime Kiln Dust	LKD
CO <sub>2</sub> Avoidance Costs	CAC	Long Rotary Kiln	LRK
Calcium Looping	CaL	Molten Carbonate Fuel Cell	MCFC
Carbon Capture & Storage	CCS	Monoethanolamine	MEA
CO <sub>2</sub> Purification Unit	CPU	Mixed Feed Shaft Kiln	MFSK
CO <sub>2</sub> Separation Unit	CSU	Parallel Flow Regenerative Kiln	PFRK
Direct Air Capture	DAC	Long Rotary Kiln with Pre-heater	PRK
Direct Contact Cooling	DCC	Alstom's Regenerative Calcium Cycle	RCC
Direct Separation	DS	Residue Derived Fuels	RDF
Electrostatic Precipitation	ESP	Selective Catalytic Reduction	SCR
Flue Gas Desulfurization	FGD	Solid-Oxide Fuel Cell	SOFC
		Selective Non-Catalytic Reduction	SNCR
		Technology Readiness Level	TRL



The composition of the limestone fed into the kiln may vary according to the specifications of the desired product, but generally requiring  $\geq 80$  wt%  $\text{CaCO}_3 + \text{MgCO}_3$  [15]. About 95% of the total energy input is employed for the calcination, which therefore reflects the key step of the process. In fact, 1.0–1.8 tonnes of  $\text{CO}_2$  are emitted per tonne of  $\text{CaO}$  manufactured, with the lime industry (not including cement manufacture) contributing for about 1% to the total  $\text{CO}_2$  emitted to the atmosphere annually [16]. The emissions from the hydration step were considered negligible here with respect to the calcination, where  $\text{CO}_2$  arises from the process chemistry (68%), fuel combustion (30%) and electricity consumption (2%) [1]. Apart from  $\text{CO}_2$ , which represents about 20 vol% of the off-gas stream, Lime Kiln Dust (LKD),  $\text{NO}_x$ , and  $\text{SO}_x$ , also arise upon calcination, with concentrations ranging between 1.4 and 2  $\text{mg}/\text{Nm}^3$  [17], 100–2000  $\text{mg}/\text{Nm}^3$  [18], and 50–400  $\text{mg}/\text{Nm}^3$  [17], respectively. While LKD represents a valuable by product which is effectively removed via modern wet scrubbers [19], both  $\text{NO}_x$  and  $\text{SO}_x$  represent a threat to human health and the environment [20]. The  $\text{NO}_x$  emissions may be limited through primary techniques (fuel selection, burner design, air staging) which prevent their formation, or secondary techniques (Selective Non-Catalytic Reduction (SNCR) and Selective Catalytic Reduction (SCR [21]), that transform the  $\text{NO}_x$  species produced into  $\text{N}_2$  and  $\text{H}_2\text{O}$ . The  $\text{SO}_x$  emissions may be limited by using fine limestone [18], injecting lime into the combustion air [19], sulfur scrubbing [10], and injecting an absorbent into the exhaust gases [18]. The composition of the exhaust off-gas stream from a lime kiln varies in accordance with the kiln, raw material feed, and fuel used for the calcination, but it can be approximated as reported in Table 1, that also shows the cement kiln off-gas, and which are quite similar.

## 2. The calcination of limestone

### 2.1. Lime industry

The choice of kiln design significantly affects the overall cost of lime production [18]; the main features of five types of kiln are reported in Table 2, where the efficiency was calculated by taking into account the theoretical energy required for the thermal dissociation of  $\text{CaCO}_3$  (1819.4  $\text{kJ kg}_{\text{CaCO}_3}^{-1}$  [22]). A deeper insight into the calcination units commercially available now follows and the technical aspects relevant

**Table 1**  
Average composition of the exhaust gases from lime and cement kilns.

Source	CO <sub>2</sub> (vol%)	O <sub>2</sub> (vol%)	N <sub>2</sub> (vol%)	H <sub>2</sub> O (vol%)
Lime Kiln Off-Gas	20.6	8.2	63.9	7.3
Cement Kiln Off-Gas	22.8	7.5	62.4	7.3

**Table 2**

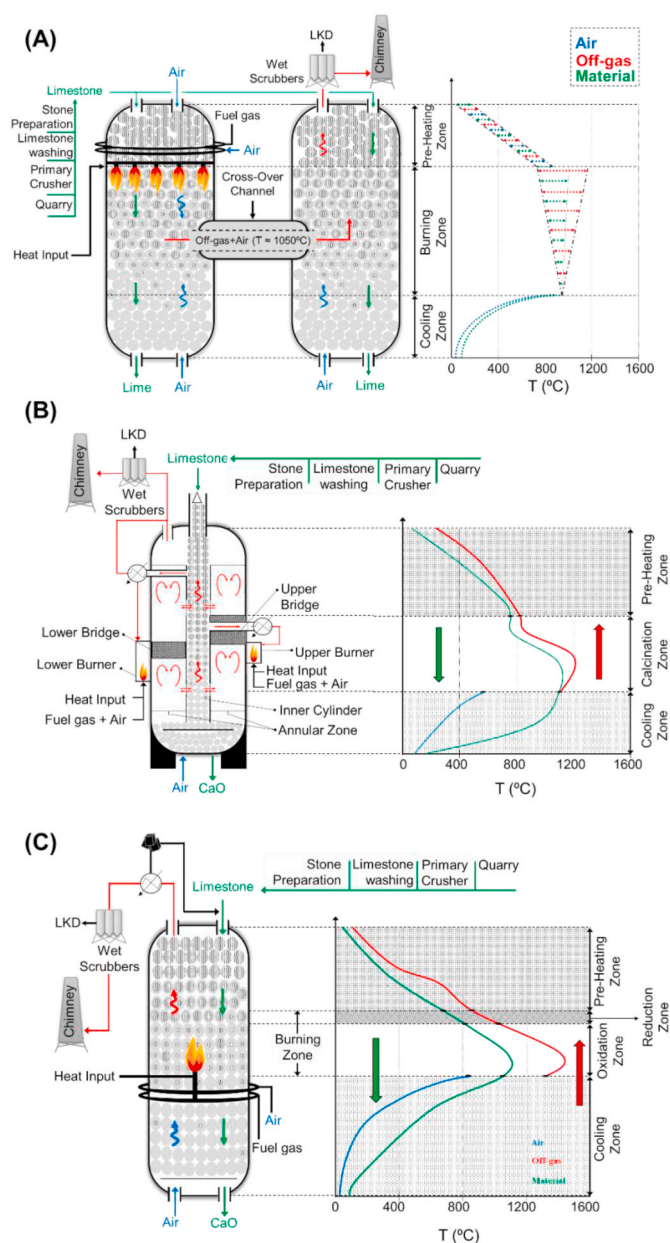
Ranges of efficiency  $\eta$ (%),  $\text{CO}_2$  emission factor, daily production and optimal feed grain size for the main kiln types used in the EU-27: Parallel Flow Regenerative Kilns (PFRK), Annular Shaft Kilns (ASK), Mixed Feed Shaft Kilns (MFSK), Rotary Kilns with Preheater (PRK), and Long Rotary Kilns (LRK).

Kiln type	$\eta$ (%)	CO <sub>2</sub> emissions factor ( $t_{\text{CO}_2}/t_{\text{CaO}}$ )	Electricity consumption (kWh/tonne)	Output range (t/d)	Input Grain size (mm)
PFRK	75–99	1.0–1.2	20–40	100–600	10–200
LRK	35–53	1.2–1.8	18–25	160–1500	2–60
PRK	41–62	1.1–1.4	17–45	150–1500	10–60
ASK	65–96	1.0–1.3	18–50	80–300	40–150
MFSK	68–93	1.0–1.5	5–15	60–200	20–200

for this discussion are outlined.

The PFRK design (Fig. 1A) represents the most used type of kiln in the EU, counting 158 units in 2013 [18]. It consists of two shaft kilns, both composed of a pre-heating (top), burning (middle), and cooling (bottom) zone. At the burning zone, the two shafts are interconnected by a crossover channel that enables very low specific heat consumption. The fuel is injected through a series of lances vertically placed in the material bed of the burning zone at the top of the first shaft, leading to combustion with the counter-current cooling air blown from the bottom. These combustion gases, together with the process  $\text{CO}_2$  released from the burned limestone, enter the crossover channel at a temperature of  $\sim 1050$  °C. These streams then flow upwards upon mixing with the cooling air from the bottom of shaft two, heating the limestone in the respective pre-heating zone. The limestone is fed at the top of both shaft kilns and slowly drops by gravity to the bottom of each calcination unit, while converting to  $\text{CaO}$ . Considering a calcination temperature between 950 and 1050 °C, the retention time of the kiln charge accounts to about 8 h [23], depending on the solid velocity set. A PFRK is suitable for different types of fuel, requiring about 20–40 kWh/tonne<sub>CaO</sub> of electrical input [18], and finally leading to a high reactivity and low  $\text{CO}_2$  residual quicklime.

An ASK design (Fig. 1B [24]) can be represented by a central cylinder, within which the limestone advances by gravity towards the bottom, passing through the pre-heating, calcination, and cooling zones. The inner cylinder is physically divided from the external shell by the so-called annular zone [25]. In the pre-heating section, the material is pre-heated by the counter-current flow of the gases arising from the upper burner, followed by proper calcination in the upper calcining zone. In the lower calcining zone, the calcination continues in a co-current flow of the limestone with the combustion gases from the lower burner. Fuel injection occurs at the height of the upper and lower burners, where the heat from the off-gas is also recovered to minimise



**Fig. 1.** Schematic overview of a PFRK (A), ASK (B) and MFSK (C) including the fluxes of the solids and gases involved, along with the temperature profile for the vertical section of the kiln. The black-pattern and light-grey circles denote  $\text{CaCO}_3$  and  $\text{CaO}$ , respectively.

energy loss. This design allows for lower thermal losses [16], with respect to PRK and LRK configurations, but it also requires longer residence times (8–20 h [26]) and higher construction costs. The lime produced presents a medium-high reactivity even when produced from a feed with poor  $\text{CaCO}_3$  content, and yields a  $\text{CO}_2$ -rich (29–34 vol%) off-gas. A limestone with average size between 40 and 150 mm is used in an ASK, which may operate continuously only at high air ratios, thereby limiting the temperature rise within the kiln. The electricity consumption is strongly dependent on the grain size, ranging between 18 and 50 kWh/tonne $_{\text{CaO}}$ . (Table 2). The raw material and the coke are mixed prior to entering the kiln, and therefore leading to a final sulfur-rich quicklime with limited quality but high reactivity.

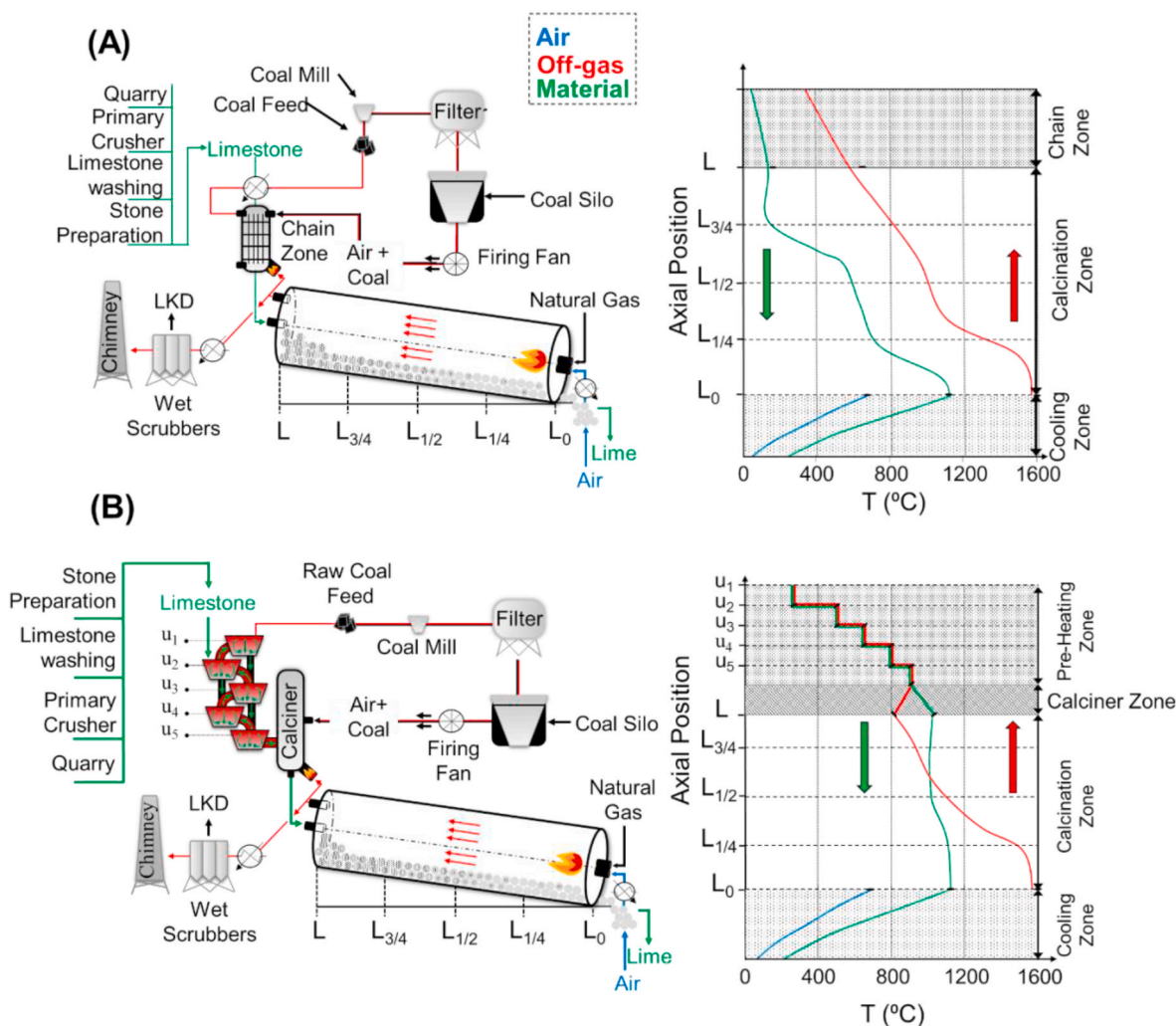
An MFSK design (Fig. 1C) is suitable for a limestone particle size in the range 20–200 mm, which moves ( $\sim 2 \text{ m h}^{-1}$ ) down the unit together with the slightly smaller and dense grade coke and anthracite, avoiding segregation. After passing through the pre-heating section, where both

the temperatures of the bed and the gas are around 800–850 °C, the feed enters the burning zone which is divided into the reduction and oxidation sub-sections. The temperatures of the flue gas and the bed range between 1000–1400 °C and 800–1000 °C, respectively, in the burning zone, while the cooling leads to a final solid product below 200 °C. The lime produced has a low-to-moderate reactivity with a high sulfur retention. Despite the low electrical consumption and construction/maintenance costs, the lifetime of the device is significantly affected by the large size of limestone fed.

The industrial LRK (Fig. 2A [27]) is normally a 50–225 m long rotating cylinder, 2–6 m in diameter, inclined at 1–4° to the horizontal, allowing the feed to move throughout the calcination unit. The limestone is fed at the upper end, in counter-current with fuel and combustion air, ensuring effective calcination of  $\text{CaCO}_3$  to  $\text{CaO}$ . Depending on the level of moisture in the feed, the process might be dry or wet; the former would involve the pre-heating and pre-calcination of the stone, and in the latter the stone is fed directly into the rotary kiln upon passage through a chain-zone. A chain system is mainly formed of oval links, ensuring better heat transfer and evaporation, together with an enhanced material transportation and decrease of dust losses from the unit [28]. Despite the higher energy efficiency linked to the dry process, it is not always convenient for existing wet-process plants to convert to dry operations, also given the humidity of the stone upon quarrying (which can be around 30%). To highlight the temperature profile within the rotary kiln, a wet process is taken into account (Fig. 2A [27]). The limestone enters the chain system at ambient temperature and leaves it at around 120–150 °C, while the temperature of the off-gas is about 600 °C. The mean residence time of the solids is 80–100 min [29], mainly depending on the rotation speed set up. Following calcination through the rotary kiln unit, the solids are collected and cooled down [30] to ambient temperature from about 1150 to 1200 °C with a counter-current ambient air flow in the cooling zone, while the off-gas is used to pre-heat both the limestone in the chain zone and the calciner fuel (shown here in Fig. 2A as coal). Strong heat losses (convection and radiation) [31] make this configuration highly energy-intensive and relatively poorly efficient ( $18\% < \eta < 25\%$ ) (Table 2), even taking into account the limited electricity consumption of 18–25 kWh/tonne $_{\text{CaO}}$  [18]. Despite this, the high flexibility and robustness, the possibility to produce limes at varying reactivity, and the feasibility for soft limestone, are possible advantages. The LRK design leads to the incorporation of the sulfur from the fuel into the produced lime, therefore rendering it suitable for a wide range of fuels [18].

A PRK is characterised by the presence of appropriate pre-heaters (cyclones, vertical shafts, and/or travelling gates) prior to the entrance of the feed into the calciner. Such a configuration (Fig. 2B [32]) ensures lower convective and radial heat losses together with improved heat recovery from the off-gases, which leave the pre-heating tower at around 200–300 °C. The temperature of the gas and the solids is quite uniform within each of a sequence of cyclones, increasing from around 300 °C to above 800 °C in the first and last units, respectively, through turbulent mixing. Following this, the solids enter the calciner, where the temperature of the solids is raised up to  $\sim 900$  °C by heat transfer from the flue and coal combustion gas, whose temperature decreases down to around 800 °C. The limestone is then fed into the rotary kiln and totally calcined for an average residence time of  $\sim 30$  min [33], leading to a final product at about 1150–1200 °C which is finally cooled down by heat exchange with a counter-current air flow in the cooling zone. Despite the higher efficiency of the PRK design respect with the LRK (Table 2), higher maintenance costs need to be highlighted. The improved heat recovery within the series of pre-heaters results in a significantly shorter length of the rotating unit (40–90 m) respect with a LRK, while a higher electrical consumption is required (17–45 kWh/tonne $_{\text{CaO}}$ ). Higher sulfur contents are detected within the flue-gas of a PRK design respect with LRK; the multiple stages of  $\text{CaCO}_3$  calcination, occurring in different units, leads to a poor sulfur uptake within the lime produced. Several adjustments may be made to prevent





**Fig. 2.** Schematic overview of a LRK (A, top) and PRK (B, bottom) design, including the fluxes of the solids and gases involved, along with the temperature profile throughout the section of the kiln. The black-pattern and light-grey circles denote  $\text{CaCO}_3$  and  $\text{CaO}$ , respectively.

excessive emissions of sulfur to the atmosphere, such as ensuring reducing conditions within the kiln, or by addition of finely crushed limestone to preferentially absorb  $\text{SO}_x$ .

## 2.2. Cement industry

The cement industry produces over 4 billion tonnes worldwide every year, of which 180 Mt are manufactured in the EU [34]. That would account for about 88 Mt of  $\text{CaO}$  produced for cement purposes annually (about four times than  $\text{CaO}/\text{Ca}(\text{OH})_2$  produced for non-construction purposes), considering a clinker-to-cement ratio of 0.81 and ~60 wt%  $\text{CaO}$  content in clinker [35]. While lime is mainly produced through the PFRK configuration for the reasons discussed above, cement is mainly manufactured within LRK and PRK units (Fig. 2A and B, respectively). Especially, the PRK configuration reflects the most energy-efficient option for clinkering, which was firstly introduced in the 1960's. Depending on the design considered, such as air-trough or air-separate pre-calciners, up to 40 and 95% of the raw feed can be decarbonised prior entering the rotary kiln [36]. It is essential that the formation of the clinker does not occur in the pre-calciner unit; therefore, around 70% of the overall amount of fuel required can be efficiently used in the pre-calciner unit.

Given both the high similarity in off-gas composition (Table 1) and process design, all the considerations discussed below assume a higher-scale importance in terms of impact, considering the much larger

market, of cement with respect to lime/slaked lime. In other words, a common approach in terms of  $\text{CO}_2$  emissions reduction may be likely adopted for the lime and cement industry.

## 3. Quicklime slaking

The hydration of  $\text{CaO}$  to give  $\text{Ca}(\text{OH})_2$  (Equation (2)) mainly involves the electrical input necessary for the handling and mixing of  $\text{CaO}$  into water (approx. 5–30 kWh consumed per tonne of hydrated lime [18]). The heat released by the strongly exothermic hydration of  $\text{CaO}$  [3] is recovered and exploited in drying the product, to produce  $\text{Ca}(\text{OH})_2$  as a powder or putty, depending on the amount of water removed by evaporation. A  $\text{Ca}(\text{OH})_2$  powder is obtained when considering a stoichiometric amount of water in the so-called “dry process”. It consists of a pre-hydrator with a double shaft paddle screw geometry, preventing caking of the product, followed by a hydrator where the  $\text{CaO}$  introduced is fully reacted with water [37]. The quality of the final product mainly depends on the limestone used, but also on the conditions applied during the hydration process [38]. A high  $\text{Ca}/\text{Mg}$  limestone would be generally hydrated under ambient conditions to give a final product with 72–74 wt%  $\text{CaO}$  and 23–24 wt% chemically-combined water content. Starting from a dolomitic limestone (35–46 wt%  $\text{MgCO}_3$ ), the hydration may be performed under ambient conditions, but  $\text{MgO}$  would remain un-hydrated [38].

Conversely, when over-stoichiometric amounts of water are used, a

Ca(OH)<sub>2</sub> putty is obtained. Different process designs may be used to perform the slaking: a slurry slaker, paste slaker, ball mill slaker, and batch slaker. A slurry slaker requires initial mixing of quicklime and water (1:3.3–5 wt ratio) in the slaking chamber; the paste flows by gravity to the grit removal chamber, where the viscosity of the slurry is reduced by addition of cold water. The grit can thus be separated at the bottom of the chamber by gravity, and finally discharged; the slaked lime will have an overall residence time of ~10 min. A paste slaker involves a lower CaO/water ratio (1:2.5), therefore is compact in size, allowing for a total residence time of ~5 min. The resulting high density requires the use of appropriate rotating paddles which push the paste toward the discharge point; here, it is diluted with four parts of water, allowing for the grit removal by gravity. Ball mill slakers are generally much more expensive than the other types, but they enable the slaking process to proceed even when the available water is highly concentrated in sulfates. An external classifier separates the slurry from the grit, which is then recirculated into the mill for further grinding and slaking. A batch slaker is a variation of the slurry slaker design, since the size of the batch reactor is predetermined and therefore the corresponding volumes of water and quicklime need to be added in succession. The slurry undergoes mixing until a temperature of 75–80 °C is achieved, then is dumped into a second tank for grit removal [39]. To prevent the reformation of CaCO<sub>3</sub> by reaction between Ca(OH)<sub>2</sub> and atmospheric CO<sub>2</sub> [40], the final slaked products resulting from all of these processes need to be stored in dry draft-free conditions.

#### 4. Sustainable solutions and research gaps

As outlined above, the calcination of CaCO<sub>3</sub> represents the key reaction for a wide range of industries, particularly lime and cement. The same chemical reaction (and thus related process engineering) is also highly relevant to the regeneration of spent sorbents in the calcium-looping carbon capture processes [41] described in section 4.1.7.

Several approaches may be considered to make this emitting process more sustainable, and this work offers the reader an overview of those possible solutions. Significant improvements have already been achieved to cut the CO<sub>2</sub> emissions arising from fuel combustion, such as fuel switching [42] and Carbon Capture & Storage (CCS) [43].

This review will also promote the fact that the thermal calcination of CaCO<sub>3</sub> is avoidable when producing lime by identifying some additional routes [44,45] which do not involve high temperatures. Such alternatives did not receive much attention yet, but the current climate crisis is urgently calling for a net change of mentality to pursue global decarbonisation. Also, the authors aim to provide a valid and strong base for all those interested in the lime industry, often overshadowed by the cement one [2,46].

##### 4.1. Carbon Capture & Storage

Although the primary focus is on power generation sources [47], CCS technologies are also believed to have high potential to mitigate the CO<sub>2</sub> emissions from a wide range of industrial processes, e.g., cement, oil refining, chemicals, glass, paper, iron, and steel production [48,49]. Post-combustion type CO<sub>2</sub> capture technologies may be a better fit for the lime industry [50], since they enable the capture of both the raw material and fuel CO<sub>2</sub>, while pre-combustion technologies could only reduce the latter category of emissions [51]. The following sections provide a detailed overview of the main CCS technologies relevant to the lime industry, highlighting the energy demand and the resulting cost of CO<sub>2</sub> removal; Table 3 below groups all the main characteristics of each solution discussed.

The CO<sub>2</sub> avoidance cost (CAC), expressed as the difference of CO<sub>2</sub>-removal costs between a plant with CCS technology and a reference plant without CCS (which may be subject to carbon taxation, although this is not explicitly included in calculations here) [60,61], is reported for each technology discussed. It is worth noting, there is no

**Table 3**

Overview of the specific energy demand and CAC (where available) for each CO<sub>2</sub> capture technology discussed in section 4.1.

Technology	Inlet CO <sub>2</sub> concentration	CO <sub>2</sub> capture rate (%)	Specific energy demand (GJ/tCO <sub>2</sub> )	CAC (€/tCO <sub>2</sub> )
Oxy-fuel [52]	18–22 mol.%	90	1.6	33 [53] - 42 [54]
RTT's PEI Solid Sorption [55]	15 vol%	90	2.7	39–46
Hollow Fibre Membrane [56]	19 mol.%	80	1.2	46–48
Veloxotherm™ RAM	–	–	–	50 [50]
CaL integrated [52]	18–22 mol.%	93	3.2	39 [57] - 59 [54]
CaL tail-end [52]	18–22 mol.%	91	4.01	52 [54]
Aker Solutions' ACC™ [58]	18 vol%	90	2.8	–
MCFC [59]	34 mol.%	31–76	0.4–1.2	–

standardised method for calculating the (CAC), therefore, we refer the reader to the individual references cited to gain further understanding on the specific assumption used in their respective calculations. The typical method for calculating the CAC is reported in Equation (3) below [54].

$$CAC = \frac{Cost_{CCS} - Cost_{ref}}{e_{eq,ref} - e_{eq,CCS}} \quad (3)$$

where,  $Cost_{CCS}$  and  $Cost_{ref}$  are the costs of the plant with and without CCS, respectively.  $e_{eq,ref}$  and  $e_{eq,CCS}$  are the specific equivalent emissions from the reference plant and the plant with CCS. However, for demonstration purposes, the application of the CCS technologies proposed will be shown for the lime industry by integrating with the PFRK calcination unit reported in detail in Fig. 1A.

##### 4.1.1. Physical/chemical absorption

The choice of a physical or chemical absorption process does not affect the quality of the lime produced, as it treats the off-stream gases and with no interaction with the Ca-based solids undergoing processing, either before or after calcination. However, the high capital costs [62] require a further implementation of the state-of-the-art technology to ensure economic return. A wide range of solvents have been investigated for liquid-phase CO<sub>2</sub> chemical absorption, including piperazine (PZ), 2-amino-2-methyl-1-propanol (AMP), aqueous ammonia (NH<sub>3</sub>), and aqueous potassium carbonate (K<sub>2</sub>CO<sub>3</sub>). Monoethanolamine (MEA) at 30–40 wt% concentration is usually considered the benchmark solvent for CO<sub>2</sub> removal [47]. Such a design can be used upon removal of SO<sub>x</sub>, NO<sub>x</sub> and particulate matter via flue gas desulfurization (FGD) [18], selective catalytic/non-catalytic reduction (SCR/SNCR) [21], and electrostatic precipitation (ESP) [63], respectively. These impurities, together with water, need to be removed prior stockage of the CO<sub>2</sub>, to prevent corrosion [64]. Moreover, the solubility of SO<sub>x</sub> as H<sub>2</sub>S in MEA and DEA has been assessed 2.4 times higher than CO<sub>2</sub> [65]; a 70% absorption of NO<sub>x</sub>-derived species, nitrate and nitrite, was observed in [66] at an NO<sub>x</sub> inlet concentration up to 150 ppm for a MEA absorber designed for a 90% CO<sub>2</sub> removal. In other words, the presence of SO<sub>x</sub> and NO<sub>x</sub> in the gaseous off-stream would also lower the absorption efficiency of the CO<sub>2</sub>, leading to a rise in removal costs. Also, the Direct Contact Cooling (DCC) prevents the degradation of the solvent occurring at the high temperature of the exhaust gases [67]. The schematic in Fig. 3A refers to the MEA-based CO<sub>2</sub> capture process for lime production proposed by Choi et al. [46], registering a promising energy consumption of 3.72 GJ/tCO<sub>2</sub> and CAC of 60–90 €/tCO<sub>2</sub>.

The off-gas leaves the PFRK unit, and it is pre-treated through wet scrubber, SNCR, ESP, FGD, and DCC, prior to entering the absorbent

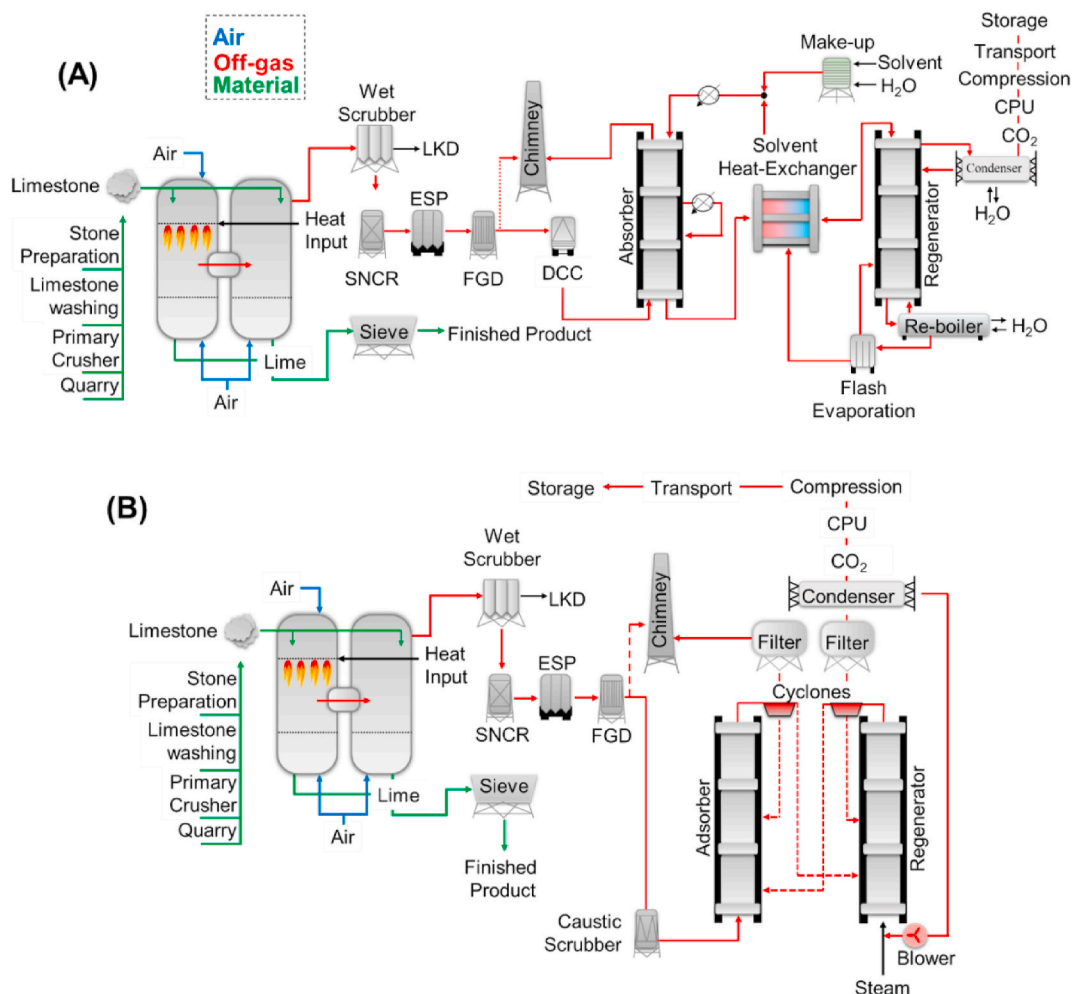
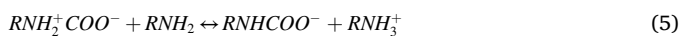


Fig. 3. Conceptual design of amine absorption CO<sub>2</sub> capture considered for lime kiln exhaust (A), and of a CO<sub>2</sub> solid sorption process considered for lime kiln exhaust (B), based on RTI and Norcem's cement pilot plant.

column as a CO<sub>2</sub>-rich gas; here, the CO<sub>2</sub> dissolves by reaction with MEA. Primary and secondary alkanolamines react with CO<sub>2</sub> to form a zwitterion ( $RNH_2^+COO^-$  in Equation (4)), which instantaneously neutralises to form a carbamate ( $RNHCOO^-$  in Equation (5)) [68]. This zwitterion mechanism does not work for tertiary amines as they cannot form a carbamate. For more information on aqueous amine and CO<sub>2</sub> chemistry see [69]. The resulting cleaned off-gas leaves the system at the top, while the CO<sub>2</sub> passes from the gas to the liquid bulk as the ionised species  $HCO_3^-$ .



The CO<sub>2</sub>-rich amine solution is then stripped in the regenerator and the reverse of reaction 4 occurs, to give a regenerated amine solution to recirculate, and a CO<sub>2</sub>-rich gaseous stream; the energy-intensive stripping of CO<sub>2</sub> from  $RNH_2$  [70] is performed through a series of re-boiling steps. These results are concordant with the 3.1–3.2 GJ/tCO<sub>2</sub> energy demand outlined from the International Energy Agency – Greenhouse Gas (IEAGHG) when considering the pulp and paper production route [71]. Currently there are no industrial or demonstration scale studies specific to solvent based CO<sub>2</sub> capture from lime kilns, whereas several demonstration-scale tests have been already reported for cement production [50,58].

The solid sorption technology has been successfully applied at RTI and Norcem's pilot-scale cement facilities, outlining relatively low CAC

of 39–46 €/tCO<sub>2</sub> [55], but also efficiency drop at higher (250 mg/Nm<sup>3</sup>) SO<sub>x</sub> concentrations. Also, by only referring to a conventional Natural Gas Combined Cycle (NGCC) power plant, a lower solvent regeneration energy (2.7 GJ/tCO<sub>2</sub> [72]) was outlined with respect to the MEA process just discussed. An example of solid sorption technology integrated with lime production in a PFRK is shown in Fig. 3B [72]. The off gas enters an absorber column upon pre-treatment via wet scrubbing, SNCR, ESP, GFD. Following the CO<sub>2</sub>-loading/unloading cycle described above for the MEA process, the CO<sub>2</sub>-rich gas from the top of the regenerator undergoes a final condensation step, leading to pure CO<sub>2</sub> and a gaseous stream which is recirculated at the bottom of the regeneration unit.

#### 4.1.2. Membrane separation

The membrane separation has not been tested yet on the exhaust gas from a lime plant, but other industrial studies highlighted promising outcomes. Specifically, the treatment of a 36 vol% CO<sub>2</sub> blast furnace gas allowed for the capture of 89% of the total CO<sub>2</sub> for an electrical consumption of 0.6 GJ/tCO<sub>2</sub> [73]. Good potential was also outlined for eventual application to the cement industry, registering an 80% CO<sub>2</sub> removal at a 40–50 €/tCO<sub>2</sub> CAC when tested at the Norcem's pilot plant [74]. Other studies [56,75] confirmed the outcomes just reported, while Lidqvist et al. [76] highlighted that the majority of the investment and operating costs of this technology are related to turbomachinery and CO<sub>2</sub> compression. Since the study considered flue gas compositions from the cement industry comparable with lime kiln exhaust gas (Table 1), it highlights the potential applicability to the lime manufacturing process.



The flow diagram in Fig. 4 was obtained by re-adapting the design in [74] to a PFRK calcination unit.

As reported, the off-gas from the kiln unit undergoes a series of pre-treatments, i.e., SNCR, ESP, and FGD, for the effective removal of water, NO<sub>x</sub>, and SO<sub>x</sub>, which would lower the efficiency of the membranes for competition effect [77]. Following, the primary CO<sub>2</sub> capture step occurs in P1 at 1.2 bar and 20–30 vol% CO<sub>2</sub>. From P1, an approximately 50 vol% CO<sub>2</sub> gas is fed into the secondary CO<sub>2</sub> capture step P2 at 1.05 bar, while a CO<sub>2</sub>-depleted (~7 vol%) stream may be emitted through the chimney. At the bottom of P2, 85 vol% CO<sub>2</sub> is directed to a compressor and finally to a CO<sub>2</sub> Condensation Column (CC), from which >99 vol% CO<sub>2</sub> at 150 bar may be obtained. The CO<sub>2</sub>-depleted gaseous streams from P2 and CC are recirculated into P1 and P2, respectively.

#### 4.1.3. Physical/chemical adsorption

Adsorption-based processes exploit the surface physical reaction between the phases involved [78], i.e. gas and solid/liquid. It is significantly different from absorption, which might be physical [79], where the solvent capacity increases almost linearly with the partial pressure of the gaseous component following Henry's law, or chemical, where a chemical interaction occurs between the reactants [80]. Adsorption-based CO<sub>2</sub> capture systems are currently close to commercialisation, however, Bui et al. [47] state that they are unlikely to compete with liquid scrubbing systems for large scale operations due to the issues related to the handling of solids. Despite this, adsorption-based systems are economically advantageous as the regeneration of the sorbent can be performed through pressure, temperature, or concentration swings, at a much lower cost than conventional amine scrubbing technologies [81]. Although no specific study of adsorption-based CO<sub>2</sub> capture systems directly applied to the lime industry could be found in the literature, interesting applications to the cement manufacturing process are reported in [50,82].

The CO<sub>2</sub>MENT project led by Svante (formerly known as Inventys) is currently in phase II of operation, aiming to capture CO<sub>2</sub> specifically from cement production, while phase III is demonstrating CO<sub>2</sub> utilisation (injection into cement and fly ash) on-site at LafargeHolcim's cement plant in British Columbia, Canada [82]. Svante's Veloxotherm™ Rotatory Adsorption Machine (RAM) uses vacuum-temperature-concentration swing adsorption in a single unit to capture CO<sub>2</sub> from cement kiln exhaust, as illustrated in Fig. 5 [82]. The device exploits the heat recovery from the PFRK unit to produce steam, which is fed counter-current with respect to the cooling air entering at the top; as a result, the off-gas entering at the bottom of the unit is split into a CO<sub>2</sub>-rich stream and a

cleaned flue-gas stream. The CAC is approximately 43 €/tCO<sub>2</sub>, and the company aims to demonstrate the first full-cycle CO<sub>2</sub> capture and utilisation attached to a cement plant [50].

#### 4.1.4. Direct Separation

This technology, exploiting the separation of the combustion and calcination reactions, has been investigated in the Low Emissions Intensity Lime and Cement (LEILAC) project through Calix's Direct Separation (DS) technology. Upon integration into the Heidelberg Cement plant in Lixhe, Belgium, CAC around 50 €/tCO<sub>2</sub> were highlighted [82, 83], therefore suggesting economic feasibility. Fig. 6A highlights the Calix DS technology design, where raw materials enter at the top of the reactor and calcined products exit at the bottom, while the process CO<sub>2</sub> rises in a counter-flow against the raw materials, allowing for the recovery of thermal energy; the resulting CO<sub>2</sub>-rich gaseous stream is cooled and exits the top of the reactor.

The limestone is indirectly heated using fossil fuels, and the remaining emissions from heating can be captured using post-combustion capture technologies or oxy-fuel combustion [84]. This innovation looks very promising since it potentially requires minimal changes to the conventional processes involved in the lime industry. The LEILAC1 pilot was completed in 2019, and due to its success [82] the LEILAC2 project plans on scaling up to demonstration scale capturing 100 ktpa of CO<sub>2</sub> [85], while also considering less carbon intensive heat sources, i.e. biomass or electricity. Additionally, grid connectivity enables the potential for this technology to balance electricity demand, stabilising the grid during highly volatile periods [85].

#### 4.1.5. Oxy-fuel

Oxy-fuel technologies are here included as an example of pre-combustion CCS alternatives; combustion is performed with high purity O<sub>2</sub> from an Air Separation Unit (ASU) and produces a CO<sub>2</sub>-rich exhaust gas from the calcination process, enabling a CO<sub>2</sub> Purification Unit (CPU) to purify and compress the CO<sub>2</sub> stream ready for storage or use. Further benefits of this technology are a consequence of: 1) limited NO<sub>x</sub> formation in the O<sub>2</sub>/CO<sub>2</sub> environment, 2) a shorter flame length, 3) an improved flame stability with Flue Gas Recycle (FGR), and 4) increased radiative heat transfer due to higher concentrations of CO<sub>2</sub> and H<sub>2</sub>O [86]. On the other hand, retrofitting plants for oxy-fuel combustion would result in major modifications to key processing units, including the need for greater sealing [87]. These modifications require long shut-down periods affecting reliability of product supply and involve very high investment costs. This last aspect may be observed in

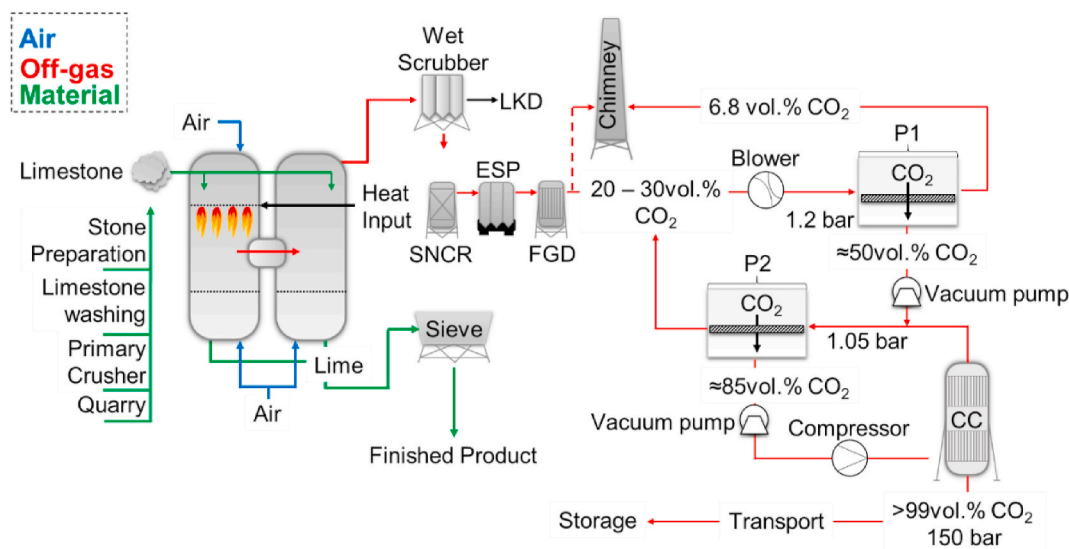


Fig. 4. Conceptual design of a membrane CO<sub>2</sub> capture considered for lime kiln exhaust, based on Norcem's pilot plant.



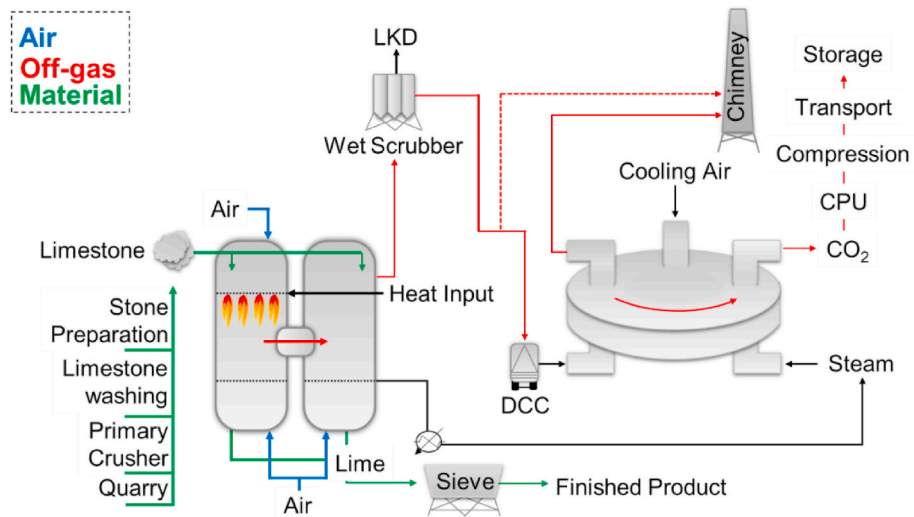


Fig. 5. Conceptual design of Svante's Veloxotherm™ RAM technology considered for lime kiln exhaust.

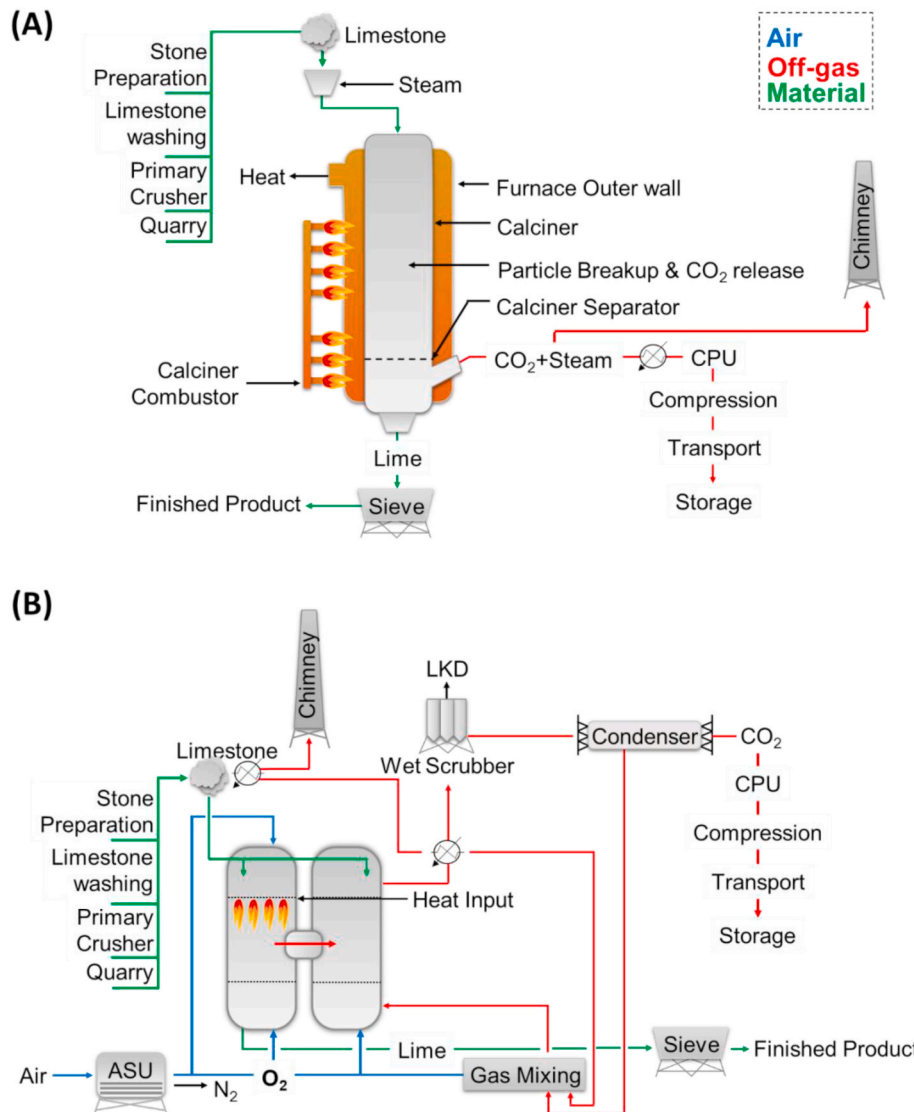
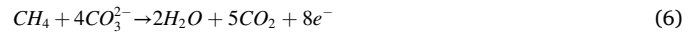


Fig. 6. Design of Calix's Direct Separation (DS) technology (A), and conceptual design of the Oxy-Fuel technology considered for lime kiln exhaust (B), using a PFRK calcination unit instead of the LRK in that study.

Fig. 6B, where the oxy-fuel combustion technology is applied to the lime industry via significant changes to the overall configuration together with the addition of a FGR [52]. Despite the expected high investment costs, very promising outcomes may be observed when oxy-fuel technology is coupled with the cement industry [88]; in fact, the oxy-fuel design showed the lowest CAC (33 €/tCO<sub>2</sub>) with the bulk of the cost associated with the ASU and CPU. Similarly, Gardarsdottir et al. [54] highlighted promising performance of the oxy-fuel process (CAC of 42 €/tCO<sub>2</sub>) when economically compared to MEA (CAC of 80 €/tCO<sub>2</sub>) and other CCS technologies, due to the lower variable operating costs and lower clinker cost. Eriksson et al. [88] used a process model to show that oxy-fuel combustion in lime kilns can produce a high-quality product with a lower specific energy demand. Similarly, Granados et al. [86] simulated oxy-fuel combustion in a lime rotary kiln, wherein their one-dimensional model showed improved heat and mass transfer rates when incorporating low levels (<65%) of FGR, indicating that smaller kiln dimensions can be used to produce the same quantity of product. At 55% FGR the lime production could increase by 13% whilst maintaining baseline operating conditions and 98% conversion. However, there is a balance required between FGR rate and decarbonisation rate, as an increased CO<sub>2</sub> partial pressure would hinder the conversion of CaCO<sub>3</sub> to CaO [89].

#### 4.1.6. Fuel cells

High temperature fuel cells, such as Molten Carbonate Fuel Cells (MCFC) and Solid-Oxide Fuel Cells (SOFC), can convert the chemical energy of a fuel directly into electricity through electrochemical energy conversion processes [90]. The applicability of the single-cell MCFC technology to the cement manufacturing process was highlighted by Spinelli et al. [59] (23.9% of the total CO<sub>2</sub> captured at 1.21 GJ/tCO<sub>2</sub>); natural gas is fed to the anode (Equation (6)), and the resulting electrical power (8e<sup>-</sup>) is used at the cathode to convert the off-gas CO<sub>2</sub> (post desulfurization) to CO<sub>3</sub><sup>2-</sup> (Equation (7)).



Following this, CO<sub>3</sub><sup>2-</sup> permeates through the electrolyte solution towards the anode, where oxygen recombines with hydrogen to give water, and CO<sub>2</sub> is regenerated. A CO<sub>2</sub>-rich stream leaves the anode towards a CO<sub>2</sub> separation unit (CSU), while a CO<sub>2</sub>-poor stream leaves the cathode and is emitted to the atmosphere upon heat recovery. Such a configuration can be considered for application to the lime manufacturing process. For demonstration, the LRK calcination unit considered in [59] is substituted with a PFRK (Fig. 7A).

Despite the low capture rate, this technology offers the potential to generate electrical and heat energy that can be internally consumed or

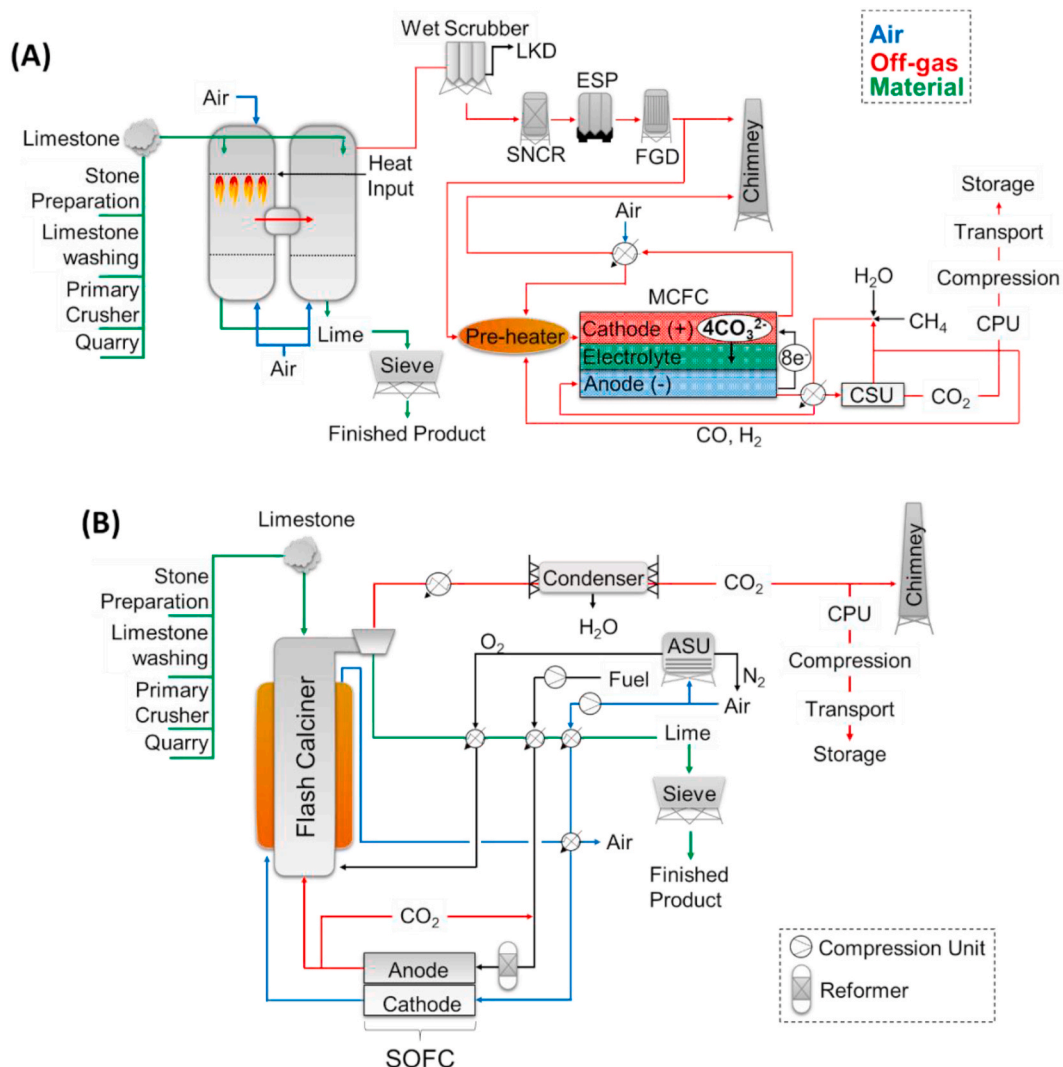


Fig. 7. Conceptual design of the MCFC considered for lime kiln exhaust (A), and Lime production integrating waste heat from SOFCs for DAC (B).

exported for profit. When using three fuel cells in series 69.9% of CO<sub>2</sub> emissions could be avoided, with a specific primary energy consumption of 0.9 GJ/tCO<sub>2</sub>; this incorporates the energy generated from the MCFC and Organic Rankine Cycle (ORC), as well as the energy demand from the CSU and compression [59].

Hanak and Manovic [91] proposed a combined heat and power generation plant using SOFCs integrated with lime production, for Direct Air Capture (DAC) of CO<sub>2</sub>; Fig. 7B shows an overview of the poly-generation process proposed. The limestone is fed into the flash calciner, where the decomposition takes place at 900 °C under pure CO<sub>2</sub> conditions, ensured by the action of the anodic chamber of the SOFC. The CO<sub>2</sub> produced at the anode (Equation (5)) is split into two streams: one is recirculated at the top of the reformer and enters the anode together with the fuel, while the other is fed at the bottom of the flash calciner. Moreover, air and oxygen are also fed at the bottom of the flash calciner, passing through the cathode and a heat exchange unit, respectively. The rising CO<sub>2</sub>-rich stream at the top of the calciner undergoes heat recovery and water separation, while the calcined material is collected upon a series of heat recovery units for the pre-heating of the oxygen, air, and fuel. The heat recovered through the air leaving the cathode ensures a high CO<sub>2</sub> concentration (>90 vol%) in the resulting gas stream, suitable for geological sequestration [92]. Despite the high capital cost (~850 €/kWh with kWh identifying the chemical energy

input) mainly due to the high cost of the fuel cell, this option may be considered economically feasible by considering the possibility of selling electricity, heat, lime, and potentially CO<sub>2</sub>.

#### 4.1.7. Calcium looping

Calcium Looping (CaL) is based on the reversible carbonation reaction from CaO to CaCO<sub>3</sub> (Equation (1)) and can be used either to remove CO<sub>2</sub> from the tail-end of the process (Fig. 8A) or integrated in the calcination step (Fig. 8B), both based on [52].

Additional fuel is required for both configurations, and incorporation of oxy-fuel combustion can be used to produce a purer CO<sub>2</sub> stream [50]. Both the configurations depicted here have been considered for cement industry by Voldsund et al. [52], highlighting lower energy demands (4.07 and 3.17 GJ/tCO<sub>2</sub> for the tail-end and integrated design, respectively) compared to MEA-based capture, but still higher than for oxy-fuel combustion. In their subsequent study [54], the CAC for the tail-end and integrated configurations was reported to be 52 and 59 €/tCO<sub>2</sub>, respectively, approximately 10 €/tCO<sub>2</sub> more expensive than the oxy-fuel combustion process. However, the calcium looping design benefits from high grade waste heat used in a steam cycle, offsetting the higher CAPEX and greater consumption of fossil fuel. It is worth noting that the effectiveness of calcium sorbents decreases with each cycle due to particle sintering during the high-temperature calcination step [93]. Such a

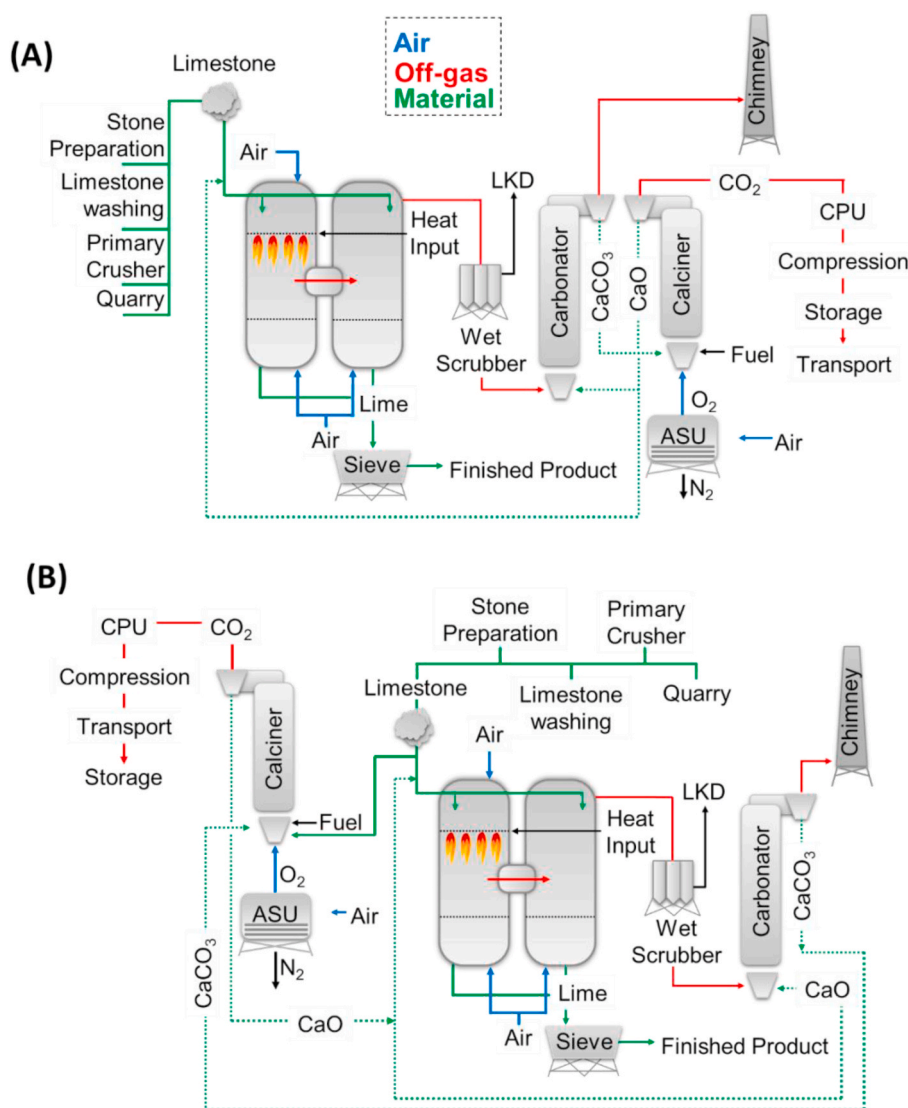


Fig. 8. Conceptual design of the Tail-end CaL (A) and Integrated CaL (B) technology considered for lime kiln exhaust.

disadvantage is mitigated with the integrated CaL process (Fig. 8B), since certain proportions of fresh  $\text{CaCO}_3$  are fed into the calciner together with the looped  $\text{CaCO}_3$ . The cyclic performance of calcium looping can be improved by incorporating regeneration of deactivated sorbents, thermal pre-treatment, using enhanced synthetic sorbents, modification of precursors, doping and including inert matrices/sup-ports [94].

Fantini [95] investigated the integrated CaL process applied to the cement manufacturing process, as part of the CLEAN clinker (CLEANKER) project, where a slipstream from the Buzzi Unicem kiln at the Vernasca cement plant (Italy) is used for demonstration. The design allowed for a >90% capture of the process  $\text{CO}_2$  from limestone, with low specific energy demand (below 2  $\text{MJ}_{\text{LHV}}/\text{tCO}_2$ ) and CAC (below 30 €/t $\text{CO}_2$ ) [95]. Another industrial demonstration performed at Norcem's Brevik cement plant [96], using GE's RCC tail-end design, reported a higher specific energy demand (3.13  $\text{GJ}/\text{tCO}_2$ ) with respect to the RCC integrated cement production with oxy-fuel combustion (1.45  $\text{GJ}/\text{tCO}_2$ ). The study also highlighted the potential for indirect heating to mitigate the power consumption and cost of the ASU [96].

#### 4.2. Fuel switching

Fuel combustion accounts for approximately one-third of the total  $\text{CO}_2$  emissions from the calcination of limestone [1,19] (as well as 60% of the overall production costs [18]); therefore, fuel switching could lead to significant emission reductions from the calcination process, e.g., biomass, but the process (i.e., raw material)  $\text{CO}_2$  produced would not be avoided.

Currently, the lime industry is mainly based on the combustion of fossil fuels such as coal, petcoke, and natural gas [18]. In contrast, many countries already use Residue Derived Fuels (RDF) in cement kilns and municipal waste incinerators, with Germany achieving an over 60% replacement of the fossil-based fuels [97]. In these terms, the biogenic carbon embodied into the waste, not counting as a direct emission since derived from biological sources, is an important factor to consider when defining the overall carbon burden of the RDF used [97]. In contrast, the recent improvements in terms of Food Waste Recycling, for which the anaerobic digestion is recognised to be the most sustainable approach, led to a lower biogenic carbon sent to incinerators and therefore resulted in a heavier carbon impact of the RDF used [98]. Several key aspects must be considered to correctly utilise the waste fuel for limestone calcining. Firstly, the choice of solid or fluid fuels may only be suitable in certain kiln types, e.g. solid lumps are not suitable for a PFRK design [23]. The processing temperature may also affect the feasibility of a certain waste fuel for a specific kiln; for instance, animal fat would solidify below 40 °C, leading potentially to pipe-plugging [99].

Other crucial factors affecting the wide usage of waste fuel for limestone calcination are the calorific power and flame temperature. Calcination requires continuous burning conditions that cannot be met if the combustion of the fuel leads to a varying thermal energy, which may happen if the waste fuel used is not sufficiently homogeneous. The impurity content also needs to be precisely specified, given that 1) limestone and the process combustion atmosphere physically interact, and the properties of the resulting lime vary due to the uptake of impurities upon calcination, and 2) the burning of specific contaminants may require systems for their removal from the off gas if they cannot (by regulation) be emitted to atmosphere. Magnetic separation is usually used for the removal of metal fragments, whose content cannot exceed certain values in the calcined material. For these reasons, the suppliers of waste fuels need to ensure precise treatment to meet relevant regulations for safe industrial use. These pre-treatments often only involve the removal of sediments or water, but in some cases chemical processes are required to remove specific pollutants. However, the gasification of waste fuels is usually performed to achieve stable combustion and avoiding the emission of  $\text{NO}_x$  and  $\text{SO}_x$  [100].

Finally, an aspect which must not be underestimated is the

availability and supply chain of the waste, since 1) a production stand-by due to an interruption in fuel supply could lead to disadvantageous economic consequences, and 2) different wastes have different calorific power and physical forms (Table 4) [101], and the process might have to be adjusted accordingly, with evident technical difficulties for continuous processes.

Despite these difficulties, the lower cost of purchase (and potentially transport) of the waste fuel compared with fossil ones, and the lower carbon footprint attributed to the energy source, can make the use of waste fuel very attractive. The combustion of wastes as fuel may also help with landfill avoidance and to mitigate waste disposal issues, because the incineration of waste leads to a 60–80% volume reduction with respect to the initial material [102], and the bottom and fly ashes resulting from the waste combustion may themselves represent a valuable material for construction purposes [103].

Another promising alternative to fossil fuels is renewable sources, which are expected to supply a significant portion of the European energy demand by 2050 [104]. Meier et al. [105] have also demonstrated the feasibility of a solar energy-powered rotary kiln for the production of sustainable quicklime. The configuration, consisting of a multi-tube reaction chamber made from high-temperature SiC panels, allowed for a 20%  $\text{CO}_2$  emissions reduction with respect to fossil fuels. The thermal calcination allowed for an overall 30–35% efficiency, comparable with the modern devices (Table 2), but the price of the calcined quicklime was about 2–3 times higher than the conventionally produced one. Recently, promising results were also obtained by Abanades et al. [89] with a Concentrated Solar Thermal (CST) technology, outlining several advantages such as no contamination from combustion, in an LRK configuration. The latest advancements have also raised other potential alternatives to fossil fuels, such as Thermal Plasma (TP) energy, obtained by passing an electric current through a gas and leading to the formation of free ions and radicals [106], and E-fuels, produced by reacting  $\text{CO}_2$  (captured from the atmosphere) with sustainable hydrogen.

Hydrogen is expected to play a crucial role for the green energy transition by 2050, given the high calorific power and the potentially net-zero emissions arising from its combustion. Depending on how the hydrogen is produced, it can be distinguished using a colour spectrum, e.g., blue, green, and grey hydrogen, indicating how sustainable the production route is [107]. "Grey" hydrogen arises from natural gas through reforming, with lower emissions with respect to coal, and when the resulting  $\text{CO}_2$  is captured and safely stored, making the overall process carbon-neutral, the hydrogen is labelled as "blue". "Green" hydrogen is completely carbon-neutral, since the electrolysis of water is conducted using clean/green electricity. There are other colours used such as black/brown (coal), pink/purple/red (nuclear), turquoise (methane pyrolysis), yellow (solar), and white (natural); however, there is no set universal nomenclature and these colour definitions could change over time, and even between regions. Apart from the widely known safety and infrastructure issues, a higher water vapour partial

**Table 4**

Calorific power (MJ/kg) and physical form of the most used waste for combustion worldwide.

Waste Type	Calorific power (MJ/kg)	Physical form
Municipal Solid Waste (MSW)	10.5	Refuse, yard, food, paper and paper-board waste.
Sewage Sludge	3.5	Solid, semi-solid and liquid waste removed during the treatment of municipal wastewater (sewage)
Medical Waste	13.9	General refuse (bedding, gauze, needles), food waste, plastics, chemicals.
Industrial Hazardous Waste	13.9	Liquids, semi-solids, tarry materials, sludge and solids
Organic Fume	1–23	Gaseous



pressure in the lime kiln (from the combustion of hydrogen), might represent a problem in terms of equipment corrosion, i.e. acid formation/condensation [108].

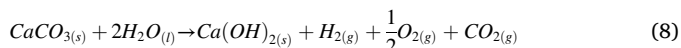
#### 4.3. Alternative production routes

The thermal calcination of  $\text{CaCO}_3$  is still generally considered to be unavoidable for industrial-scale lime production, and therefore higher-technology readiness level (TRL) research has focused on capturing  $\text{CO}_2$  via post- and pre-combustion CCS technologies. However, major challenges need to be overcome in order to successfully apply CCS technologies to industries where the calcination of  $\text{CaCO}_3$  represents a key processing step.

In the next sections, we will be exploring novel (lower-TRL) "cold" routes for the synthesis of  $\text{Ca(OH)}_2$  that avoid the thermal treatment of  $\text{CaCO}_3$ . The first alternative involves an electrochemical synthesis of  $\text{Ca(OH)}_2$  from  $\text{CaCO}_3$ , with simultaneous production of  $\text{O}_2/\text{CO}_2$  and  $\text{H}_2$  gases; although the process  $\text{CO}_2$  would still be emitted as a gas, the high volumetric concentration would ease its separation from the remaining gases in a CCS process, potentially resulting in a more affordable process. The second alternative route involves a room-temperature liquid-solid reaction between  $\text{CaCO}_3$  and  $\text{NaOH}$  solutions to give the products  $\text{Ca(OH)}_2$  and  $\text{Na}_2\text{CO}_3 \cdot x\text{H}_2\text{O}$  ( $x = 0, 1$ ). In other words, the process  $\text{CO}_2$  from  $\text{CaCO}_3$  would be sequestered in a stable mineral form ( $\text{Na}_2\text{CO}_3 \cdot x\text{H}_2\text{O}$ ), leading to a potential zero-emissions slaked lime production, although the carbon burden linked to  $\text{NaOH}$  usage still needs to be considered in order to assess the environmental impact of the process. Since both the alternative routes mainly rely on electrical power, to be discussed below, the carbon footprint attributed to the generation of electricity will play a key role in determining their sustainability. It is also worth noting that calcination-free production of calcium hydroxide from alkaline waste (e.g., fly ashes and slags) at sub-boiling temperatures has also been developed [109]; however, these sources are in limited supply compared to  $\text{CaCO}_3$  and are being phased out.

##### 4.3.1. Electrochemical decarbonisation of $\text{CaCO}_3$

An electrochemical decarbonisation of  $\text{CaCO}_3$  was presented by Ellis et al. [44], who used a water electrolyser and chemical reactor to convert  $\text{CaCO}_3$  to  $\text{Ca(OH)}_2$ , under potentiostatic conditions (cell voltage 2.5 V, current 6 mA). The maximum yield (coulombic efficiency) was calculated by considering the molar stoichiometry depicted in Equation (8), and it was assessed to be 0.85.

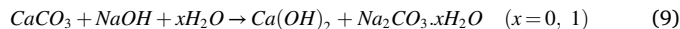


Since 1 mol of  $\text{H}_2$  is produced for each mole of  $\text{CaCO}_3$  initially fed, a large portion of the total energy demand might be fulfilled in situ; this aspect must be clearly assessed, given that it could make the process even more attractive from an industrial point of view.

Although the process  $\text{CO}_2$  could not be avoided, the authors [44] also outlined promising applications allowing for its recovery, together with the co-generated  $\text{O}_2$  and  $\text{H}_2$ . For example, the  $\text{O}_2/\text{CO}_2$  gaseous stream resulting from the anode (67 vol%  $\text{CO}_2$ ) may be applied via oxy-fuel technology in a conventional lime manufacturing process, leading to lower energy consumptions and  $\text{NO}_x$  emissions, as outlined in Section 2.1.6. Such an application would lead to an exhaust kiln gas that is highly concentrated in  $\text{CO}_2$ , enabling significant efficiency improvements of the eventual CCS process. Alternatively, those gases could be used to power a SOFC [110], generating electrical energy that is required in other process steps such as mixing and grinding. As a further consequence, the  $\text{O}_2/\text{CO}_2$  gas stream would be further enriched in  $\text{CO}_2$ , facilitating the separation and compression steps. Although the authors [44] focussed on the potential for cement production, the electrochemical decarbonisation of  $\text{CaCO}_3$  also fits the process specifics of the lime industry.

##### 4.3.2. Chemical decarbonisation of $\text{CaCO}_3$

Another non-combustion route to decarbonisation of  $\text{CaCO}_3$  was firstly introduced by Hanein et al. [45], involving the reaction between solid  $\text{CaCO}_3$  and  $\text{NaOH}$  solutions at atmospheric conditions and varying concentrations; the key reaction is reported in Equation (9).



This alternative decarbonisation of  $\text{CaCO}_3$  avoids both the fuel and process  $\text{CO}_2$  emissions, since no combustion would be required. The  $\text{CO}_2$  from  $\text{CaCO}_3$  would also be sequestered in a stable mineral form ( $\text{Na}_2\text{CO}_3/\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ ), and  $\text{Ca(OH)}_2$  produced simultaneously in a single step, rather than via  $\text{CaO}$ . The process is fast and requires minimal mixing energy [111]. In addition, no additional treatments of  $\text{CO}_2$  compression, transport and storage would be required, since most of the  $\text{CO}_2$  involved in the process would be solidified as  $\text{Na}_2\text{CO}_3 \cdot x\text{H}_2\text{O}$ . The relatively simple reaction setup offers promising scope for eventual up-scaling, based upon achievement of the highest conversion efficiency (96%) linked to the optimal ( $\text{CaCO}_3:\text{NaOH}:\text{H}_2\text{O}$ ) mix design [45]. This alternative route is still at a laboratory level, and an overall reassessment of the markets of  $\text{Ca(OH)}_2$  [112],  $\text{Na}_2\text{CO}_3$  [113] and  $\text{NaOH}$  [114] must be achieved for the route to succeed in substituting the calcination of  $\text{CaCO}_3$ . Also, it must be mentioned that the chlor-alkali process necessary for the supply of  $\text{NaOH}$  [115] is currently a carbon-intensive process, with 0.78 tonne of  $\text{CO}_2$  emitted per tonne  $\text{NaOH}$ , if fossil fuels are used in its production [116]; the co-generation of  $\text{H}_2$  is already included in the energetic calculation. Therefore, a pre-requisite for feasibility of a "low-carbon" classification for this alternative route to the production of slaked lime will be low emissions from the  $\text{NaOH}$  industry, which is strongly expected to cut the emissions by using green/renewable electricity [117] for the sustainment of the chlor-alkali process.

## 5. Concluding remarks and recommendations

The environmental burden attributed to the lime industry is mainly related to the thermal calcination of  $\text{CaCO}_3$  to give  $\text{CO}_2$  that may be distinguished by the nature of its origin: process  $\text{CO}_2$  embodied in  $\text{CaCO}_3$  and released upon thermal degradation ( $\sim 68\%$ ), fuel combustion  $\text{CO}_2$  ( $\sim 30\%$ ), and  $\text{CO}_2$  arising from electricity consumption ( $\sim 2\%$ ). To date, consistent results have been achieved to limit the emissions from the combustion process itself, for instance by design optimisation and process efficiency, to minimise energy wastage, and/or by using alternative fuels with a lower carbon footprint. Despite this, the process  $\text{CO}_2$  remains the main challenge we face to effectively reduce the emissions, as long as the thermal decarbonisation of  $\text{CaCO}_3$  is viewed as the only practical option to obtain  $\text{CaO}$ . In these terms, the application of CCS technologies to treat the arising off-gas stream is considered the best option towards a decarbonised lime industry, but further optimisation is required. If only the CAC and  $\text{CO}_2$  capture rate were to be considered, the Oxy-fuel technology would represent the best option to develop. Despite that the Horizon 2020 CEMCAP included Oxy-fuel among those CCS technologies with high potential in retro-fitting [118], its adaptation to the existing lime plants appears unlikely in a short-to-mid-term scenario. In fact, the very high capital costs discourage the prompt dismantling of the state-of-the-art lime plants, whose typical lifetime is between 30 and 50 years [118]. For this reason, the MEA absorption process is still outcompeting all the other configurations, representing the most solid route with no requirements for design change of the existing plants. The high energy demand required for the regeneration of the solvent requires a strong implementation of the technology, which could consider 1) other solvents with more convenient regeneration conditions or 2) the use of renewable sources and optimised heat recovery from the kiln to minimise the carbon burden linked to the combustion of fuels required for the regeneration step. These obstacles are pushing towards the implementation of the other designs described above, among which are the membrane separation and solid adsorption. A high potential is associated with the former option, which has been

positively tested for industrial sources with higher (steel) and comparable (cement) CO<sub>2</sub> concentrations in the off-gas stream, with respect to the lime process. No literature sources for the lime production route could be found, suggesting that a specific case-study should be done in order to test the feasibility for the industry in exam here. The solid adsorption represents a valid alternative to the similarly structured MEA process, given the lower energy required for the regeneration of the adsorbent. Although, the handling of the solids represents an additional energy expenditure, which must be considered by also looking at the service life of the adsorbent, shortened by events of sintering occurring at multiple cycles of regeneration. The same issues can be found for Ca-looping, which offers a valid and retro-fittable alternative for a sustainable lime production, but that still needs to overcome the technical issues linked to a relatively short service life of the looped CaCO<sub>3</sub>/CaO upon sintering and decreasing of the reactive surface. The use of fuel cells also looks promising, given the lowest energy demand detectable among the solutions considered, but the low capture rate requires a series of MCFs for an effective CO<sub>2</sub> removal. That would increase both the initial investments and the maintenance costs associated with the multiple devices required. Said that, particular attention must be paid prior feeding the flue gas to the fuel cell, in order to avoid issues linked to a high temperature and the presence of foreign species lowering the efficiency and service time of the device.

Consistent investments are required to ease the application of targeted CCS technologies on a short-term basis, whereas the current trend would only allow for a gradual transition towards novel designs. Specifically for the lime industry, more specific pilot-scale research is expected, in order to not rely on the similarities with the cement manufacturing process.

Further possibilities were recently inspired by two separate studies by Ellis et al. [44] and Hanein et al. [45], who conceptualised innovative alternative routes for a cold/no-combustion decarbonisation of CaCO<sub>3</sub>. Both lines of investigation inspire new points of view on the matter, since the avoidance of the thermal calcination of CaCO<sub>3</sub> has not previously been demonstrated in a scalable manner, and both processes could allow production of H<sub>2</sub> as by-product (depending on system boundaries). Both the alternatives may have the potential to influence the future lime and cement supply chain, if deeply investigated and fully scaled-up. Realistically, a total transition towards a no-combustion lime production is currently unlikely, but these alternatives might eventually provide a valid alternative for a partial supply of the lime market. While the eventual feasibility of the electrochemical route mainly relies on the cost of electricity, the chemical alternative also depends on other industrial realities, such as soda ash and caustic soda, whose demands would need to be adjusted accordingly. Specifically, an increased caustic soda production will be required to sustain the process, whereas the co-production of sodium carbonate should be translated in a re-sizing of the conventional Solvay manufacturing route. All these assumptions make the evaluation of these alternatives challenging, and it requires the concerted transition of both industrial and energetic markets. However, further implementation of alternative fuels will be the baseline for the realistic application of the most CCS technologies discussed and will also sustain the novel no-combustion approaches presented here.

This review highlights the potential for alternative approaches to the standard lime manufacturing process, mainly regarding the aspect of the process CO<sub>2</sub>. A powerful hint has been offered to the scientific community, which is now called upon to prove the techno-economic feasibility of alternative cold decarbonisation processes, potentially allowing for a net-zero emissions lime industry. Lime is also a well-known absorbent of CO<sub>2</sub> (as discussed in Sections 1. and 4.1.7.); therefore, the no-carbon production of lime can enable carbon neutrality of other hard-to-abate sectors. This is a window of opportunity for the lime industry, as its livelihood may be threatened suddenly if high-temperature kilns, as we know them, are required (by legislation or by societal pressure) to be phased out to reduce impacts of global climate change.

## Author's contribution

Marco Simoni and Mathew D. Wilkes drafted the original manuscript. Theodore Hanein, Hajime Kinoshita, John L. Provis, and Solomon Brown acquired funding, and supervised Marco Simoni and Mathew D. Wilkes. Theodore Hanein, Hajime Kinoshita, John Provis, and Solomon Brown reviewed and edited the manuscript.

## Declaration of competing interest

The authors declare that they have no competing interests as defined by Renewable & Sustainable Energy Reviews, or other interests that might be perceived to influence the interpretation of the article.

## Data availability

No data was used for the research described in the article.

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