1 Introduction

1.1 Research background

CO_2 emissions in the production of lime

Lime (CaO) is an important product used in construction and building, iron and steelmaking, treatment of water and gaseous effluents, agriculture, the food industry, and the chemical industry [1,2]. It is produced through the calcination of limestone (mainly $CaCO_3$) at temperatures between 900 and 1200 °C. This process is highly endothermic and requires the combustion of fuels such as gas oil, coal, coke, or some types of secondary fuels (e.g. oil, plastics, paper) [3]. CO_2 emissions from combustion, known as *combustion CO_2 emissions*, can be reduced by replacing fossil fuels with renewable fuels such as biomass. *Process CO_2 emissions*, resulting from the decomposition of $CaCO_3$, account for approximately 65% of total CO_2 emissions and can only be avoided using CO_2 capture [4]. Overall, the total CO_2 emissions per ton of burnt lime vary between 1 to 2 t_{CO2}/t_{lime} [3]. Due to the nature and high level of CO_2 emissions, CO_2 capture, utilization, and storage (CCUS) is fundamental to decarbonize the lime production [5].

Only a few studies have analyzed CO_2 capture technologies specifically for the lime industry [6–9], whereas many works have been published recently that consider carbon capture for the cement industry (e.g., [10–12]). There are similarities between both industries, like the calcination of $CaCO_3$, which is the main process in terms of energy consumption [3]. Moreover, CO_2 capture from cement and lime plants have many common features. In both production processes, most of the CO_2 emissions come from the raw material, and the specific CO_2 emissions per unit of product are approximately the same. The other components of the flue gas (e.g., HCl, SO_2, moisture, NO_x and N_2, and residual dust) are also comparable if the same fuels are used [3]. A robust process is needed in both cases to capture the CO_2 from the flue gases. Even though this work focuses on the CO_2 capture from a lime plant, reference studies on carbon capture from cement kilns are used for comparison purposes. The production of lime and cement is responsible for around 8 % of global anthropogenic CO_2 emissions [13].

The entire carbon capture and storage (CCS) value chain for preventing CO_2 from being emitted into the atmosphere consists of separation, purification, transport, and geological storage of CO_2. Alternatively, CO_2 can be captured and utilized (CCU), e.g., to produce chemicals. CO_2 utilization has been proposed as an alternative to permanent storage. However, utilizing CO_2 is likely to serve as a minor complement. The scale of emissions reduction needed to decarbonize the industry is expected to rely mainly on CCS [14].

There are many means to transport CO_2, such as rail tankers and trucks [15]. For large-scale transportation, pipelines are the best option, but more research is required to better understand the impact of impurities (e.g., H_2O, O_2, H_2S) and mature this technology. The lowest costs are achieved when CO_2 is transported in pipelines as a dense-phase fluid, i.e., above the critical pressure and below the critical temperature [16], typically at 100 bar and ambient temperature [17]. Ships have been used for over 30 years to transport CO_2 and are a good alternative for large distances. The optimal condition for CO_2 transportation via ships is cryo-compressed at 15 bar and −30 °C [18].

CO_2 can be sequestered through mineral, oceanic, or geological storage [15]. The latter is the most proven sequestration method. Among the several options of geological CO_2 storage, enhanced oil recovery (EOR), and injection into saline formations [19] are the most mature. Currently, tens of facilities store CO_2 via EOR [20]. Recent commercial-scale projects such as Gorgon CO_2 Injection (Australia) and Quest CCS (Canada) store CO_2 in saline formations [16].

The latest report of the Intergovernmental Panel on Climate Change (IPCC) states that net-negative CO_2 emissions are required to achieve net zero greenhouse gas (GHG) emissions [21] and cap global warming to 1.5 °C with no or limited overshoot [22]. This strategy, known as *carbon dioxide removal* (CDR), is a “key element” to limit global warming because it is the only means to counterbalance the so- called “residual emissions”, i.e., uneconomical to abate anthropogenic GHG emissions [23]. Emission scenarios compatible with the 1.5 °C limit (67 % probability) require huge amounts of CDR on top of deep emissions reductions; namely, 730 Gt_{CO_2} on average [22,24]. One of the most promising ways to achieve net-negative CO_2 emissions is the implementation of CCS into industrial processes that emit high amounts of biogenic CO_2. This approach is called bioenergy with carbon capture and storage (BECCS) [23,25]. BEECS can help decarbonize the production of lime and cement and deliver negative CO_2 emissions at competitive costs [26].

The capture process is the most energetically demanding step of the entire CCS chain, accounting for about 70–80 % of the total costs [27,28]. The main research projects on CO_2 capture from lime and cement industries of the last years were the LEILAC project, the CEMCAP project, the CLEANKER project, and the ANICA project [29–31]. Many more research projects to advance CO_2 capture technologies for lime and cement plants are currently running [14], while several industrial-scale capture projects for cement plants have been announced [26]. Since this dissertation focuses on CO_2 capture, we provide a more detailed discussion of this step below.

CO_2 capture technologies

Different classifications for CO_2 capture technologies have been proposed [32,33]. In this dissertation, we adopt the following classification, according to the overarching separation approach [15]: (i) pre-combustion, (ii) oxy-fuel combustion, (iii) post-combustion, and (iv) integrated industrial separation. Most studies agree on the first three. Approaches (i) to (iii) are suitable for capturing CO_2 from power plants [34]. Capturing CO_2 from industrial production, such as cement and lime plants, can be performed using oxy-fuel combustion (ii), post-combustion capture (iii), or fully integrated capture technologies, such as those relying on indirect calcination (iv). A special approach, known as direct air capture (DAC), involves extracting CO_2 directly from the atmosphere [35]. It is a flexible technology capable of achieving net-negative CO_2 emissions [36]. However, it comes with significantly higher costs compared to other capture methods, due to the much lower CO_2 concentration in the gas phase from which CO_2 is extracted (i.e., the atmosphere).

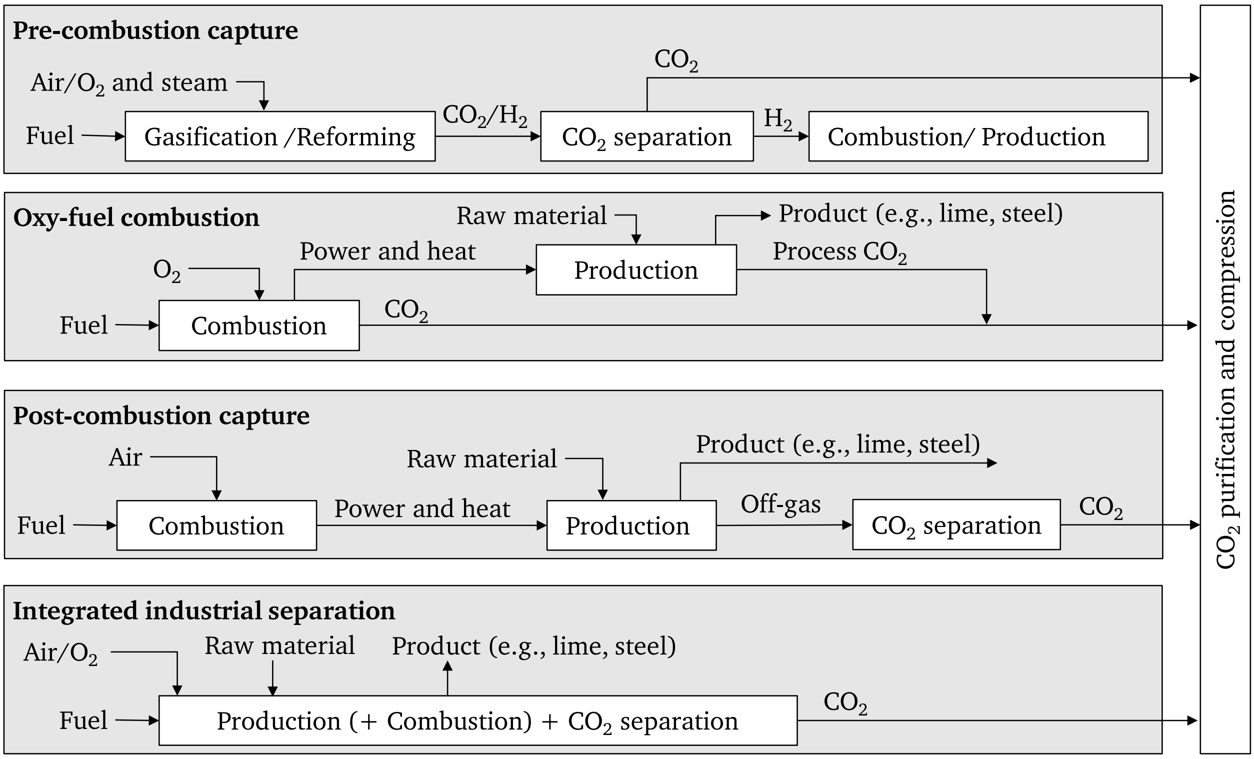

Figure 1. CO_2 capture technologies categorized according to the overarching separation approach, adapted from [15,37].

Figure 1 illustrates the four overarching approaches to capture CO_2 from industrial sources. After the separation, further processing, including compression, dehydration, and purification is usually required to comply with the requirements of transport and storage, or utilization [38,39].

Pre-combustion CO_2 capture consists in converting coal, natural gas, heavy oil fractions, biomass, or waste-derived fuels into a gaseous mixture composed mainly by CO and H_2 (synthesis gas) [33]. The main routes to produce synthesis gas are the gasification of solid or liquid fuels, and the reforming/partial oxidation of gaseous fuels [40]. The yield of H_2 can be increased by reacting CO with steam in a water-gas-shift reactor. If the CO_2 is separated and permanently stored, the synthesis gas is a carbon-free energy carrier. The separation can be performed using either physical or chemical absorption processes, cryogenic separation, or solid physical adsorption (pressure swing and temperature swing). Physical absorption methods, such as Rectisol®, are viable for pre-combustion capture due to the relatively high CO_2 concentrations (15–60 vol%) before the separation step, which also helps reduce equipment costs [28]. Pre-combustion CO_2 capture has been proposed for power generation in a combined cycle. This approach is known as integrated gasification combined cycle (IGCC) technology. Using pre-combustion CO_2 capture technologies in industrial production can only avoid fuel-related CO_2 emissions, but not process CO_2 emissions [26]. This is why, in practice, this approach is not applicable to lime and cement industries.

The Quest CCS facility is a commercial example of pre-combustion CO_2 separation, which currently captures and stores approximately one million tonnes of CO_2 per year in Canada. Commissioned in 2015, this facility uses a pre-combustion process to separate ca. 50 % of the CO_2 generated during hydrogen production.

Oxy-combustion technology is based on the combustion of fuels using pure oxygen instead of air to avoid diluting the CO_2 of the flue gases with N_2 [33]. It allows to obtain highly concentrated CO_2 streams ($> 80\ \text{vol\%}_{\text{wb}}$). This approach, which was originally proposed for combustion systems, is also suitable for capturing CO_2 from industrial processes (industrial separation), such as cement plants [41].

Eriksson et al. [6] studied oxy-fuel combustion in a lime rotary kiln. They found that with this system, the total CO_2 emissions may be reduced, but pointed out technical challenges to control the temperature and, in this way, comply with the high-quality standards of rotary-kiln lime products. The high environmental and economic potential of oxy-fuel combustion for cement production has been highlighted by different authors [42,43]. Carrasco et al. [44] investigated oxy-fuel carbon capture from cement production in a 500 kW_{th} testing facility. This technology has good energy performance and high potential for low CO_2 avoidance costs, which have been calculated at approximately 42 $€/\text{t}_{\text{CO2,av}}$ for cement production [45]. However, significant retrofitting challenges may hinder its economic feasibility [46].

Within the *GeZero* project, an oxy-fuel cement kiln will be built in at a Heidelberg Materials facility in Geseke, making it the first commercial cement plant in Germany with full-scale CO_2 carbon capture and storage [26]. The objective of this project is to capture 700 $\text{kt}_{\text{CO2}}/\text{y}$ starting in 2029. Additionally, an oxy-fuel pilot plant is being constructed in Mergelstetten, Germany, as part of the *catch4climate* project [47]. This semi-industrial plant will use an oxy-fuel process developed by thyssenkrupp Polysius. Commissioning is scheduled for the beginning of 2025.

Post-combustion systems separate CO_2 from flue gases downstream of combustion [33]. The CO_2 concentration in the combustion gases is generally 3–15 vol% but higher concentrations are possible in off-gases of industrial processes. Different separation techniques can be deployed in post-combustion CO_2 capture, such as absorption in liquid sorbents, membrane separation, adsorption-desorption processes, and cryogenic capture [15]. However, the majority of them have high thermodynamic and economic penalties [46,48–50].

Absorption technologies are well-established but require considerable heat for sorbent regeneration and the used sorbents have potential negative effects on the environment [51]. Among them, amine-based CO_2 capture technologies are more suitable for retrofitting than oxy-combustion and have high technology-readiness levels [46]. However, most amine absorption technologies have very high energy requirements, which increases the costs of CO_2 capture and significantly reduces system efficiency [52]. Gardarsdottir et al. [45] evaluated different post-combustion carbon capture processes for cement production. They calculated that monoethanolamine (MEA) absorption, the reference post-combustion carbon capture technology, has a specific primary energy consumption for CO_2 avoided (*SPECCA*) of 7.0 $MJ/kg_{CO2,av}$ and a cost of CO_2 avoided of 80 $€/t_{CO2,av}$. Barker et al. [43] calculated CO_2 avoidance costs exceeding 100 $€/t_{CO2,av}$ for retrofitting a 1-Mt/y cement plant in Northeast Scotland with a solvent-based post-combustion capture unit. Membrane separation offers high market accessibility but presents operational challenges such as fouling, and significant expenses when high capture efficiencies are needed [51]. Membrane separation technology is sometimes regarded as a competitive alternative to decarbonize the lime and cement industries, but it is still costly ($>$ 80 $€/t_{CO2,av}$) if capture rates of more than 80 % are to be achieved [45,53,54]. Adsorption processes face significant energy penalties associated with the desorption step required to regenerate the adsorbent. While cryogenic separation has extensive operational experience, it is only economically viable for high CO_2 concentrations, due to the substantial energy costs associated with cooling. The carbonate looping (CaL) process, which is the predecessor of the capture process analyzed in this dissertation, is a promising post-combustion CO_2 capture technology that can be deployed in the lime industry [55]. It is discussed in the following subsection.

The Petra Nova CCS plant captures approximately 90 % of the CO_2 emissions from a coal-fired power plant in Texas (USA). The CO_2 is separated from the rest of the flue gas with the KM CDR post-combustion process from Mitsubishi Heavy Industries, which employs a proprietary amine developed by the company. The CO_2 is compressed, transported, and utilized for enhanced oil recovery (EOR), permanently sequestering it underground. This project was commissioned in the year 2017. After a 3-year shutdown, the plant has been operational since September 2023.

Currently, a capture facility using an amine-based capture process developed by Aker Carbon Capture is being built at a cement plant in Brevik, Norway [56]. The heat for regenerating the sorbent will be obtained from electrical power and waste heat recovery from the cement process and the CO_2 compression. After separation, the CO_2 will be liquefied and transported via ships to the storage location in the North Sea. It will be the first industrial-scale CO_2 capture plant in the cement industry worldwide, with an annual capture rate of 400 kt_{CO2}/y. Commissioning is planned for 2025.

After Brevik, the Edmonton CCUS project represents the most advanced development in carbon capture within the cement industry, aiming to avoid 1 Mt_{CO2}/y [57]. This project involves retrofitting a post-combustion amine capture system and a combined heat and power plant into a cement production facility operated by Heidelberg Materials in Canada. The combined heat and power plant is crucial to the project's economic viability. The final investment decision is anticipated by early 2025.

The project CalCC, which started in 2023, aims to construct the first CO_2 capture facility at a commercial lime plant [58]. The Lhoist Group's Réty lime plant in France will be retrofitted with a Cryocap FG unit, from Air Liquide. The Cryocap technology captures CO_2 at very high purity using cryogenic temperatures. The captured CO_2 will be transported via an 80-km pipeline, shared with other industrial streams, to the Port of Dunkirk. The CO_2 will then be liquefied and shipped to a location in the North Sea for permanent geological storage.

Integrated industrial separation technologies use indirect heating or electrification to capture CO_2 from hard-to-abate industries. One promising integrated technology to decarbonize the lime industry is the direct separation of the LEILAC project (low emissions intensity lime and cement), which uses an indirectly heated vertical tube for the calcination [59]. This technology has been demonstrated at a scale of 240 t/d of raw meal, separating 85 t/d of CO_2. A scale-up of this technology will take place within the LEILAC-2 project, aiming to capture 100 kt of CO_2 per year [60]. Direct separation enables the capture of all process emissions at a low cost [61], but it cannot separate the CO_2 produced by combustion. The fully integrated indirectly heated carbonate looping process [62], which is analyzed in this dissertation, is another example of integrated industrial separation.

Carbonate looping technology

One of the most promising CO_2 capture technologies for lime and cement plants is the *carbonate looping* (CaL) process [63], which operates based on the reversible carbonation-calcination reaction of CaO [64,65]. CO_2 is captured through the carbonation of CaO in a *carbonator* operating at ca. 650 °C—see Eq. (1). Since the carbonation is an exothermic reaction, the reactor needs to be cooled and the reaction heat can be recovered, e.g., in a steam cycle.

$$\mathrm{CaO\,(s) + CO_2\,(g) \rightarrow CaCO_3\,(s)};\ \Delta H_{298\mathrm{K}} = -180\ \mathrm{kJ/mol} \tag{1}$$

The sorbent is regenerated through calcination in a *calciner* operating at higher temperatures (ca. 900 °C)—see Eq. (2). Heat needs to be provided to the calciner because of the endothermic nature of the reaction.

$$\mathrm{CaCO_3\,(s) \rightarrow CaO\,(s) + CO_2\,(g)};\ \Delta H_{298\mathrm{K}} = +180\ \mathrm{kJ/mol} \tag{2}$$

Due to the different reactor temperatures, the equilibrium CO_2 partial pressure ($p_{\mathrm{CO2,eq}}$) changes, enabling carbonation in the carbonator, and calcination in the calciner. Figure 2 illustrates the variation of $p_{\mathrm{CO2,eq}}$ with the operating temperature (T), highlighting the regions corresponding to carbonation (lower T) and calcination (higher T). For operating conditions relevant to the CaL process, $p_{\mathrm{CO2,eq}}$ is generally calculated with Eq. (3), which was obtained by García-Labiano et al. [66] based on thermodynamical data from Barin [67]. This correlation agrees remarkably well with those reported in previous empirical studies [68].

$$p_{\mathrm{CO2,eq}} = 4.137\,10^{12}\,\exp\frac{-20474}{T + 273.15} \qquad [\mathrm{Pa}] \tag{3}$$

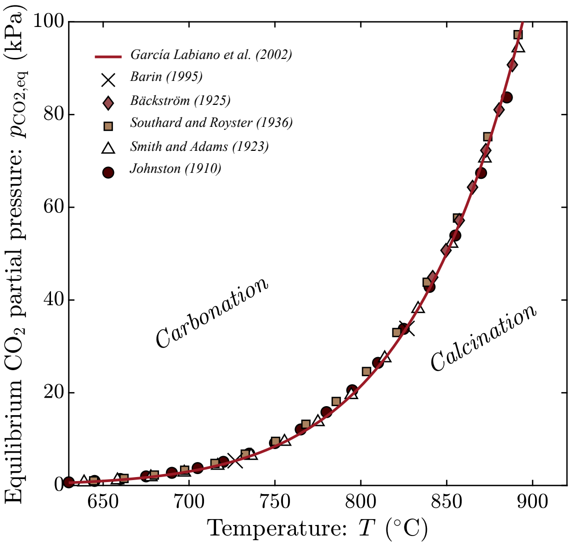

Figure 2. Equilibrium CO_2 partial pressure for carbonation-calcination calculated using the correlation from García Labiano et al. [66]. Results from historical correlations [68] derived from empirical data are plotted with markers only for their range of validity. Values calculated using thermodynamical data from Barin (1995) [67] are indicated with a cross (×). Adapted from RP VI.

On account of its high operating temperatures, the CaL process allows for various efficient heat integration strategies, including power generation through heat recovery. Additionally, the raw materials used in cement and lime production can function as sorbents in the CaL process, while spent sorbents can be recycled as feedstocks for lime and cement plants. These advantages significantly enhance the energy utilization of the process, enabling efficient CO_2 capture without incurring high costs [69,70].

Figure 3 illustrates the CaL process schematically. The solid sorbent, lime (mainly CaO), circulates between the carbonator and the calciner, both operating as fluidized bed reactors [71–73]. Concepts involving entrained flow reactors have also been proposed [74,75]. In the carbonator, CO_2 from off- gas reacts with the sorbent to form $CaCO_3$—see Eq.(1). The carbonated sorbent is regenerated in the calciner and CO_2 is released in a high purity stream—see Eq. (2). In the standard configuration, the heat for the calcination is provided via oxy-fuel combustion, directly in the calciner, using pure oxygen and fuel (see [76]). A fraction of the captured CO_2 is recirculated back into the calciner to achieve optimal fluidization velocities and control the reactor temperature. The sorbent's capacity to capture CO_2 declines rapidly during the initial calcination-carbonation cycles [77], due to loss of porosity caused by sintering [78]. To sustain sorbent activity at acceptable levels, fresh limestone (make-up) is introduced into the system, while spent material is removed (purge).

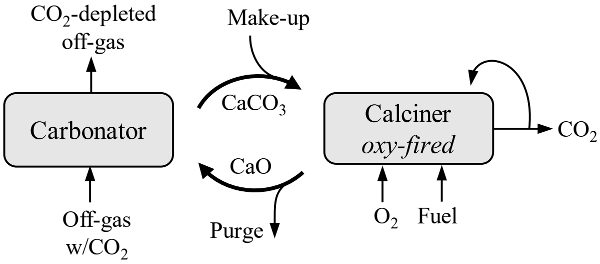

Figure 3. Scheme of the oxy-fired carbonate looping (CaL) process.

One significant drawback of standard CaL technology is the requirement of pure oxygen, which is obtained with an energy-intensive air separation unit (ASU). The installation of an ASU entails significant investment. De Lena et al. [69] calculated that the ASU accounts for around 15 % of the total plant cost for an integrated CaL system for CO_2 capture from a cement plant. A similar result was obtained by Fu et al. [79] for the implementation of the CaL process in natural gas combined cycle plants. Additionally, the electric power required to operate the ASU can exceed 40 % of the total electricity demand of the CaL system, including compression and purification [69,80].

For power plants, the CaL process has the potential to achieve high CO_2 capture rates with low energy penalties. Lasheras et al. [81] estimated that a full-scale power plant could be retrofitted with CaL to capture 88 % of the total CO_2 formed, with an energy penalty of less than 2.9 %. Astolfi et al. [82] calculated that a specific primary energy consumption for CO_2 avoided (*SPECCA*) of 2.2 $MJ_{LHV}/kg_{CO2,av}$ could be achieved by the integration of the CaL process into power plants with thermochemical energy storage, and Haaf et al. [80] estimated a *SPECCA* of 5.7 $MJ_{LHV}/kg_{CO2,av}$ for the integration into waste-to-energy plants. De Lena et al. [69] investigated the application of different CaL configurations in the cement industry. They reported *SPECCA* values between 2.8–3.0 $MJ_{LHV}/kg_{CO2,av}$ for systems utilizing pure limestone as sorbent, and between 3.5–4.6 $MJ_{LHV}/kg_{CO2,av}$ for systems that utilize cement raw meal.

Santos and Hanak [83] reviewed the available techno-economic analysis studies on carbon capture for industrial processes of the last ten years. They concluded that CaL is superior to other CO_2 capture technologies for this kind of application. According to their estimations, CaL technology has average CO_2 avoidance costs of 33 to 43 €/$t_{CO2,av}$ and an equivalent energy requirement between 2.0 and 3.7 $MJ_{th}/kg_{CO2,av}$. De Lena et al. [84] analyzed carbonate looping technology for cement plants and obtained slightly higher costs (52–59 €/$t_{CO2,av}$) for their scenarios. Romano et al. [85] presented an integrated concept for cement production and power generation that would be profitable even for low carbon taxes, starting at 27 €/t_{CO2}.

CaL technology has been demonstrated up to the pilot scale for manifold operating conditions [86], including firing with waste-derived fuels [87]. CO_2 capture rates higher than 99 % in CaL operations have been reported [88]. Since the beginning of the last decade, extensive experimental work has been conducted in semi-industrial facilities [86]. The oxy-fired CaL process has been demonstrated in many pilot tests. The major test facilities are located in Stuttgart (200 kW_{th}) [89–91] and Darmstadt (1 MW_{th}) [92,93], Germany; La Pereda, Spain [94,95]; and Heping, Taiwan

(1.9 MW_{th}) [96]. Firing various types of fuels in a CaL calciner was successfully demonstrated, including hard coal and lignite [97], solid recovered fuels [98], and biomass pellets [88]. Recently, Magli et al. [99] achieved over 90 % capture efficiency at a pilot facility built *in situ* at a cement plant in Vernasca, Italy, which features a 105-meter entrained-flow carbonator [100].

The indirectly heated carbonate looping process

The efficiency penalty of the CaL process can be further reduced by eliminating the need for oxygen in the calciner [101]. This can be achieved by using steam [102–104] or solar energy [105,106] for sorbent regeneration, or by electrifying the calciner, employing plasma burners, electrical resistance, or induction [107–109]. Another alternative is to indirectly heat the calciner by combustion of fuels in an external *combustor*. This promising approach is known as the *indirectly heated carbonate looping* (IHCaL) process (see Figure 4). Heat can be transferred into the calciner by means of metallic walls [59,110], by solids circulation [111,112], or via heat pipes [101,113]. Heat pipes offer an excellent heat transfer performance based on evaporation and condensation of a liquid, i.e., sodium for temperatures > 800 °C, inside a closed pipe [114].

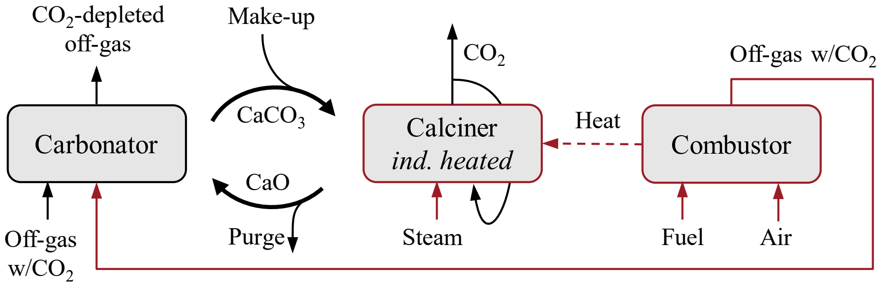

Figure 4. Scheme of the indirectly heated carbonate looping process (IHCaL). Differences with the CaL process are highlighted with red borders.

Figure 4 illustrates the IHCaL process with heat pipes. The operating principle is analogous to that of the oxy-fired CaL process (see Figure 3), with solid sorbent (CaO) circulating between a carbonator and a calciner to separate CO_2 into a high-purity stream. Heat from an external combustor is transferred to the calciner via heat pipes. For the fluidization of the calciner, steam, recirculated CO_2, or a mixture of both may be used (cf. [115]). The flue gas from the external combustor is directed to the carbonator, where most of the CO_2 is captured by carbonation. To ensure efficient heat transfer, the calciner and the combustor operate as bubbling bed reactors, with heat pipes immersed in the fluidized beds.

The main advantages of the IHCaL process compared to the standard CaL process are summarized as follows [62,116]:

- No air separation unit is needed to produce pure oxygen, which leads to lower investment costs and lower energy consumption.
- Fewer impurities (sulfur, ash) from a supplementary firing are brought into the Ca-loop, so that spent sorbent will be of higher purity and therefore be better suited for further utilization.
- Lower CaO deactivation rates are expected due to “mild” calcination around the heat pipe surfaces compared to rather harsh conditions in an oxy-fired calciner so that sorbent remains more reactive.
- Lower attrition rates are expected due to a low fluidization velocity in the calciner, which improves the operability of the fluidized bed system.
- An almost pure CO_2 stream leaves the calciner, which allows for technically easy and cost-effective CO_2 purification for storage/utilization of CO_2.

The IHCaL concept using heat pipes has previously been evaluated for CO_2 capture from coal-fired power plants [114]. CO_2 avoidance costs have been calculated at 23 €/t_{CO2} [116], excluding

CO_2 transport and storage. Until the start of the work leading to this dissertation, the IHCaL process had only been considered for power plant applications [114,116] but not for lime or cement plants. The CaL and the IHCaL processes can be integrated into the lime industry using waste-derived fuels or biomass, thus enabling negative CO_2 emissions (CDR) through bioenergy with carbon capture and storage (BECCS) (e.g., [117]).

Pilot testing of the IHCaL process

To date, the only pilot tests of the IHCaL process using a heat-pipes heat exchanger [114] were performed in a 300-kW_{th} pilot facility at the Technical University of Darmstadt, Germany [118]. This pilot facility, commissioned in 2015, is illustrated in Figure 5. It is composed of three reactors: a carbonator for CO_2 capture, a calciner for sorbent regeneration, and a combustor for heat generation. The carbonator is an eight-meter-high circulating fluidized bed (CFB) with an internal diameter of 250 mm. It is fluidized using a synthetic flue gas composed of air, CO_2, SO_2, and H_2O. The calciner is a bubbling bed (BFB) fluidized with air, featuring a mean particle residence time of ca. 20 min. The height of the bed is determined by the solid outlet, which is located 1.9 m from the bottom of the reactor. The external combustor is a BFB operating with sand. Heat is transferred from the combustor into the calciner via 72 heat pipes. A *cone valve* is located downstream of the carbonator to control the sorbent circulation rate. Solid sorbent can be extracted discontinuously from the cone-valve arrangement for sampling. A detailed explanation of the experimental setup can be found in previous publications [119–122]. Recently, this plant has been expanded with a gas tract to feed the combustor's flue gas into the carbonator and capture its CO_2 [121].

Several test campaigns have been conducted at this pilot facility, totaling ca. 700 hours of operation [123]. The tests included operating conditions relevant to power plants [120], and lime and cement plants [119]. Recently, Hofmann et al. [121] operated the IHCaL facility by co-firing propane with both dried lignite and refuse-derived fuel.

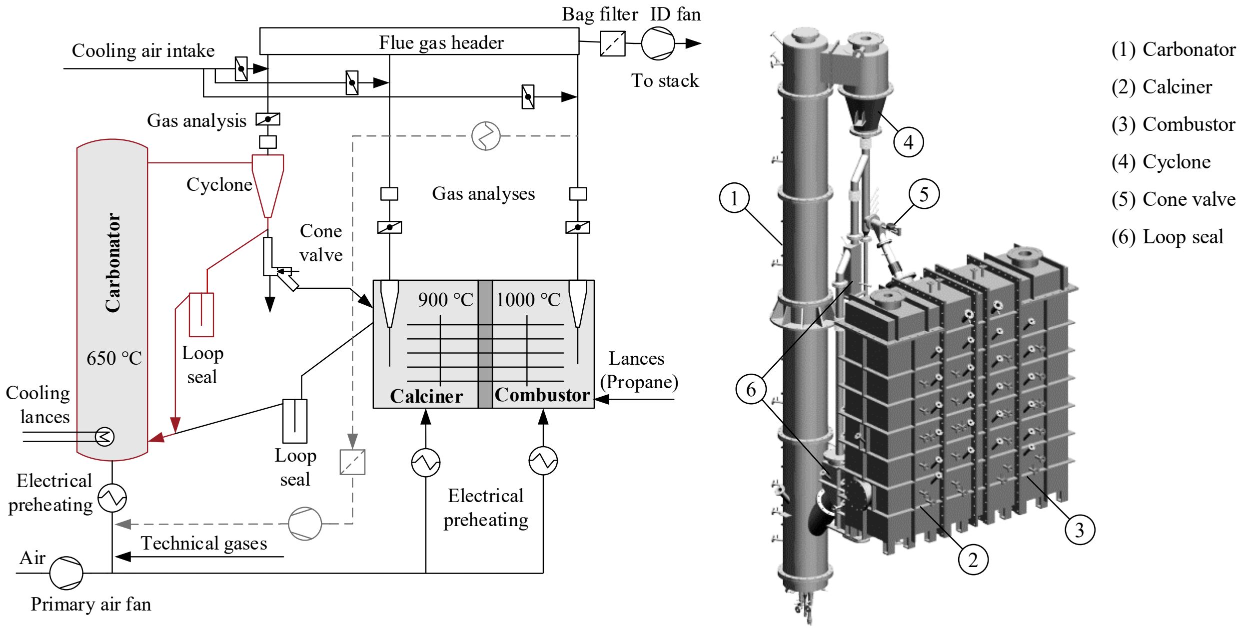

Figure 5. Pilot plant at the Technical University of Darmstadt for testing the indirectly heated carbonate looping (IHCaL) process at the 300-kW_{th} scale. The left subfigure is a process flow diagram adapted from RP IV. The main reactors are shaded in gray. The new flue-gas tract commissioned in 2022 are indicated with light-gray broken lines. The carbonator with its internal circulation is indicated with red borders. The figure on the right is a render of the CAD model illustrating the reactors and the components for solid circulation (adapted from [120]).

1.2 State of the art

Until the start of this dissertation, experimental efforts to develop IHCaL technology have been unparalleled by modeling work. However, alongside reliable empirical results from semi-industrial facilities, accurate models are essential for interpreting experiments and scaling up IHCaL technology for commercial application. This section reviews the current state of IHCaL development for lime plants, focusing on the aspects most relevant to this dissertation: process integration and modeling. Based on the limitations of previous studies, we identify the key research needs that led to the research questions outlined in Section 1.3.

Integration of IHCaL technology in the lime production

There are many potential synergies between the IHCaL process and the production of lime and cement. Cement raw meal and limestone, the primary materials in cement and lime production, can serve as sorbents for the IHCaL process, and spent sorbents can be repurposed as raw materials to produce cement and lime. Additionally, the heat and electrical energy demands of cement and lime plants offer opportunities for heat recovery. Moreover, the common practice of using waste-derived fuels in the cement industry, when combined with IHCaL technology, can enable net-negative CO_2 emissions.

Given the large quantity of CO_2 emissions associated with the lime and cement production (see Section 1.1), large-scale capture plants are necessary. This scale is attractive for IHCaL technology, which is CAPEX-driven and therefore benefits considerably from economies of scale. The CO_2 concentration in off-gases from lime plants is generally higher than the CO_2 concentration in flue gases from power plants, which affects the process by influencing reactor performance and energy requirements.

Despite the high potential of IHCaL technology for capturing CO_2 in the lime and cement industries, no integration concepts had been developed prior to this cumulative dissertation. Integrating the IHCaL process into cement and lime production plants was one of the goals of the ACT ANICA Project [124]. Integrating it into cement production was carried out by a project partner (cf. [125]), while we focused on the integration into lime production, a primary topic of this dissertation. Many of the methods developed and conclusions drawn from our study on lime plants may also be applicable to integrating the IHCaL process into cement plants.

Modeling of the IHCaL process

Accurate reactor models are essential for assessing sorbent performance, interpreting experimental findings, designing optimized reactors, and safely scaling up IHCaL and CaL technology for commercial applications [126]. Carbonator and calciner models include considerations on reactor behavior (reactor sub-model), as well as sorbent kinetics and deactivation (particle sub-model). Complete process simulations are commonly performed using Aspen Plus [127] (e.g., [81,128]). Some of the reactor models can be integrated into Aspen Plus process models using customized FORTRAN routines (e.g., [81]), which considerably enhances the reliability of the process simulations. The steam cycles may be modeled with EBSILON professional [129] (e.g., [130]).

Carbonator reactor sub-models are abundant in the literature [126]. Most of them simulate circulating fluidized bed carbonators, which are the most established reactor type for the CaL and IHCaL processes. Some models assume continuous stirred-tank reactor (CSTR) operation [73,131,132]. They have the advantage of being easy to calculate but do not account for the influence of reactor hydrodynamics on the capture process, which leads to high uncertainties (cf. [133]). Other models are based on three-dimensional CFD simulations [134–136], which can predict empirical data well, but require considerable computational resources, which makes them impractical for many applications, especially modeling of big reactors. One useful modeling approach is the so-called *Kunii and Levenspiel* (KL) reactor model for fluidized beds [137], which considers two phases (gas and solid) for the simulations and uses semi-empirical equations to model the solids distribution and the gas-solid contact behavior [138]. KL models provide good results with less computational effort than three-dimensional CFD models [126] (cf. [134]). Therefore, they can be easily integrated into global models of CaL systems. There are many KL-type carbonator models in the literature. Lasheras et al. [81] developed a model based on semi-empirical equations from Kunii and Levenspiel [139] and particle models from previous works [72,140]. They assumed that the sorbent entering the carbonator was fully calcined. Their model overpredicted empirical data for some operating conditions of the 1-MW$_{th}$ CaL pilot plant at the TU Darmstadt [93]. Romano [141] developed a carbonator model considering a particle *residence time distribution* (RTD) for the calculation of sorbent deactivation and carbonation reaction rates. Although his results presented reasonable agreement with experimental data, he reported a systematic overestimation of the capture efficiency. Ylätalo et al. [142] used a one-dimensional model to evaluate the performance of a carbonator, considering an axial temperature gradient across the height of the reactor. The results they obtained were consistent with experimental results from a CaL laboratory test rig (30 kW$_{th}$) during steady-state operation. Their model relied on a *back-flow ratio*, which was not disclosed. It is uncertain whether their accurate predictions are based on a fitting process specific to the laboratory operating conditions. Recently, Tizfahm et al. [143] developed a model that considers reaction kinetics and reactor hydrodynamics. However, they only validated the kinetic sub-model with experimental data, not the KL reactor model. Most KL carbonator models lack a comprehensive discussion of their methodology. Furthermore, new models often build upon old ones without scrutinizing underlying assumptions. For instance, solids distribution profiles are usually adopted from previous works without analyzing the fluidization regimes for which they are valid. Something similar occurs with the constants for the calculation of core-wall gas interchange and the equations to obtain the reactor gas-particle contact efficiencies.

There are still issues that need to be investigated to enable the commercialization of CaL and IHCaL. One of the unanswered questions is how fluidization regimes influence carbonator behavior. Charitos et al. [73] compared two CaL test rigs and reported high CO_2 capture rates for facilities operating in different fluidization regimes. However, they pointed out that the reactors operating in the turbulent fluidization regime presented better gas-solid contact. Recently, Diego and Arias [144] reported experimental results from a 1.7-MW$_{th}$ CaL pilot facility showing that the carbonator performance was better for lower gas velocities. Still, there has been no investigation of the fluidization regimes of CaL carbonators using appropriate explanatory models.

Carbonator particle sub-models are essential for linking sorbent kinetics and carrying capacity to reactor behavior, which are heavily influenced by sorbent make-up and circulation rates. These factors play a critical role in determining capture efficiency, as widely recognized in the literature [126,145,146]. However, experimental and modeling results often exhibit contradictions across different studies. Furthermore, previous assumptions are generally incorporated into new models without critically assessing the studies on which they are based. This issue is not consistently addressed when incorporating particle sub-models into carbonator models.

Considering the interconnectedness of the carbonator and the calciner is essential for developing a comprehensive CaL model. High calcination temperatures should be avoided to prevent damage to the heat pipes and minimize energy penalties. Conversely, excessively low temperatures can result in poor calciner performance, thereby compromising CO_2 capture efficiency. Therefore, a precise model of the calciner's influence on carbonator operation is crucial.

Numerous studies have identified difficulties in attaining high calciner performance. Rodríguez et al. [147] highlighted low calcination efficiency as a potential cause of reduced carbonator performance in a 30-kW$_{th}$ CaL test facility. Haaf et al. [98] reported a reduction in calciner efficiency associated with low calcination temperatures in a 1-MW$_{th}$ CaL pilot plant using waste-derived fuels and oxygen to fire the calciner. Reitz et al. [120] disclosed difficulties in achieving high calcination efficiencies in a 300-kW$_{th}$ indirectly heated test rig. Recently, Hofmann [148] identified poor calcination performance as a critical factor contributing to low capture efficiency in the IHCaL plant at the TU Darmstadt. Despite reported challenges in achieving high