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A flexible CO₂ capture system for backup power plants using Ca(OH)₂/CaCO₃ solid storage

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CO₂ capture technologies are required to address intermittent sources of CO₂, such as the natural gas combined cycle (NGCC) used for backup power applications. The high reactivity of Ca(OH)₂ powder facilitates the design of low cost carbonators to capture diluted CO₂ (typically below 4%_v in NGCC flue gases) as CaCO₃. By storing CaCO₃ and Ca(OH)₂ it is possible to decouple the CO₂ capture step in the carbonator from the oxy-calcliner/hydrator block in which Ca(OH)₂ is regenerated and CO₂ extracted. This facilitates the integration of CO₂ capture elements in backup power systems. Simulations of the completely integrated backup power plant with and without capture indicated that for a NGCC capacity factor (CF) of 0.1, the thermal capacity of the oxy-calcliner was just 2% of the gross power output of the NGCC gas turbine. Capture efficiencies of 90% can be reached without modifying the operating conditions of the gas power plant, while achieving a global efficiency of 38% for the system with CO₂ capture. A basic economic analysis indicated that the proposed scheme would lead to a cost of CO₂ avoided of approximately 200 \$ per tCO₂, making it suitable for retrofitting natural gas-based power plants.

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1. Introduction

To achieve zero emissions by 2050, carbon-free backup power systems and/or large-scale energy storage are required for those periods of time with low and/or intermittent renewable resources.^{1–3} Among them, natural gas combustion turbines could be used as backup systems owing to their rapid response to changes in load and demand, as well as their low thermal stress during start-up.^{4,5} However, CO₂ produced during the operational periods of these backup turbines needs to be captured in order to minimize CO₂ emissions.^{6,7}

Most of the developed CO₂ capture technologies, generally complex and capital-intensive, present sub-systems originally designed only for base-load operation. Therefore, even if the technical complexities associated with their dynamic operation are resolved, they will face prohibitive costs when operated under low capacity factors (CF), as expected in backup systems based on natural gas (*i.e.*, CF of 0.1–0.2). This has been recognized as a weakness of CO₂ capture technologies, and recently there is growing interest in more flexible CO₂ capture processes. In previous studies,^{8–11} calcium looping (CaL) was already investigated as a suitable capture technology to address the challenge of capturing CO₂ from intermittent sources. In CaL systems, CaO reacts with the CO₂ present in a flue gas to produce CaCO₃ and a “free”-CO₂ flue gas, and then the carbonated solids are regenerated *via* calcination for further cycles while producing a CO₂ stream ready for storage.¹² The use

of inexpensive limestone as a CO₂ sorbent precursor (CaO) allows the steps of the CO₂ capture process (carbonation and sorbent regeneration) to be decoupled^{8–11} by integrating a CaO/CaCO₃ solid storage system. Although this type of approach may be suitable for coal-fired power plants, where the CO₂ content in the flue gas is 10–15%_v, the CaL technology is less effective for CO₂ capture from gas turbine flue gases with a typical CO₂ content of 3–4%_v.¹³ In these cases the capture efficiency is limited by the CaO + CO₂ ↔ CaCO₃ equilibrium to values below 80% when the carbonator operates at standard temperatures around 650 °C as the CO₂ equilibrium concentration is 1.2%_v.¹⁴ Although studies on the integration of CaL systems with natural gas combined cycle (NGCC) power plants are scarce, most propose reducing this carbonation temperature to avoid equilibrium restrictions and achieve higher CO₂ capture efficiencies.^{15–18} However, when the carbonation reaction temperature is reduced, the CO₂ carrying capacity of the CaO sorbent decreases drastically^{19–21} and the carbonation reaction rate declines.²² As a result, increased solid circulation rates between the carbonator and calciner are needed for a given CO₂ capture target. Also, the lower carbonation conversion of the CaO solids will require increasingly large solid storage volumes in the flexible CO₂ capture system.⁸

To address the above-mentioned rate and conversion limitations, the use of finely powdered Ca(OH)₂ (with a particle size of a few microns) as a CO₂ sorbent has been proposed as an alternative to CaO^{23–26} by including an additional hydrator reactor in the standard CaL system (comprising only the carbonator and calciner reactors). It is recognized that Ca(OH)₂ presents much faster carbonation kinetics, higher conversion in

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the temperature range of 500–650 °C even under low CO₂ concentrations and high stability maintained along cycling.^{23,24,27} As a result, the sorbent and make-up flow requirements are minimized and more compact carbonator reactors with reduced gas/solid contact times can be used.²⁸ For this application, and considering the small particle size and poor fluidization properties of Ca(OH)₂, entrained bed gas–solid reactor configurations, similar to those used commercially for dry flue gas desulfurization,²⁹ and pre-calciners, as those used in cement plants,³⁰ could be used for the CO₂ capture step and the calcination of the carbonated sorbent, respectively. Moreover, other reactor configurations such as multiple cyclonic reactors³¹ could also be proposed. However, the use of Ca(OH)₂ as a sorbent instead of CaO results in thermal penalties linked with its low carbonation enthalpy (+72 kJ mol⁻¹ at 650 °C). Thus, the amount of heat that can be recovered from the carbonator is considerably lower than that of standard CaL systems using CaO as a sorbent. In addition to this, the flue gas needs to be introduced to the carbonator at temperatures above 500 °C to ensure high carbonation conversion within short reaction times.²⁸

Most of the previous studies reported in the literature on Ca(OH)₂-based CaL systems^{23,25,26} are aimed at capturing CO₂ from fuel-fired power plants operated at base load with high capacity factors. For these processes, the carbonator, calciner, and hydrator reactors are directly interconnected and continuously operated to capture CO₂ in steady state mode.^{23,25,26} So, in this work the integration of a flexible CaL system based on Ca(OH)₂ to capture CO₂ from a NGCC power plant, which is operated as a backup power system, is investigated. The proposed flexible Ca(OH)₂-based CaL system uses an intermediate storage of CaCO₃ and Ca(OH)₂-rich solids to decouple the CO₂ capture step from the sorbent regeneration step.³² The objective of the process integration study is to minimize the energy penalty during short periods when backup power is required while shifting the energy penalties to periods of low-power demand. A basic economic analysis is performed to estimate the cost of CO₂ avoided of the proposed system.

2. Process description

A general scheme of the CO₂ capture process evaluated in this study is shown in Fig. 1, coupled with a state-of-the-art NGCC power plant. This process is similar to those of other CaL

systems that are adapted to backup power plants based on CaO, including the carbonator and calciner reactors integrated with a sorbent storage system to decouple the CO₂ capture and sorbent regeneration steps.^{8,9,11} Solid silos, similar to those commercially available on a large scale for the cement and lime industries,³⁰ can be used as suitable sorbent storage systems. Moreover, an additional hydrator is included to produce Ca(OH)₂ from the CaO solids leaving the oxy-calciner so the CaL system benefits from the advantages of Ca(OH)₂ as an efficient and rapid CO₂ sorbent.

As stated in the Introduction section, the use of Ca(OH)₂ presents certain drawbacks due to the lower carbonation enthalpy and the higher temperature required for the gas entering the carbonator. In the proposed system, the first problem is compensated by the simplicity of the carbonation step. Thus, the carbonator is considered as an adiabatic reactor with no heat recovery in the steam cycle (*i.e.*, without heat transfer surfaces to recover the heat released during the process). This facilitates the operation of the power plant and carbonator (especially during start-up and shut-down periods) and reduces the cost associated with the CO₂ capture equipment, which typically results in a large economic penalty during operation under low CFs. The second problem is addressed by integrating the carbonator between the exit of the natural gas turbine and the inlet of the heat-recovery steam generator (HRSG), as discussed in the following section. This is similar to previous base-load steady-state NGCC-CaL systems proposed in the literature.^{16–18} Moreover, the temperature required for the gas entering the carbonator (*i.e.*, above 500 °C) conveniently corresponds to the typical turbine outlet gas temperatures, which are in the range of 580–640 °C.³³

In the proposed system, when the backup NGCC power plant enters into operation, the flue gas leaving the gas turbine is fed into the carbonator, where it is contacted with Ca(OH)₂ from a storage silo to react with the CO₂ present in the flue gas. At the carbonator exit, the carbonated solids are separated from the decarbonized flue gas and stored in another silo. Subsequently, the decarbonized flue gas is sent to the NGCC power plant to recover the heat contained in this stream in the HRSG section (not shown in Fig. 1 for simplicity) before being released to the atmosphere.

In contrast to the intermittent operation of the NGCC power plant and carbonator, the sorbent regeneration block (right-hand side of Fig. 1) is operated at a steady state. Thus,

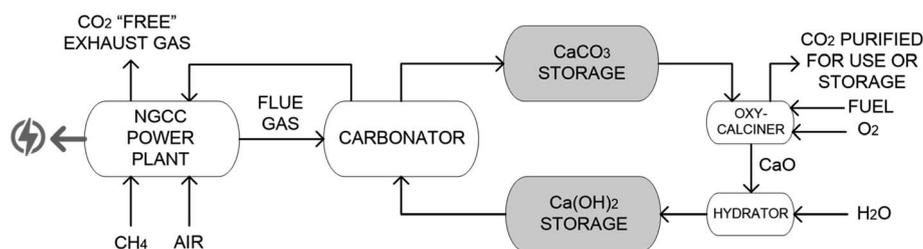


Fig. 1 Schematic of the highly flexible backup NGCC power plant with CO₂ capture using a CaO/Ca(OH)₂/CaCO₃ loop, including Ca(OH)₂ and CaCO₃ storage silos.



a continuous flow of CaCO_3 -rich solids from the storage silo is continuously calcined in the oxy-calciner, where fuel is burned using O_2 . Then, the CaO solids separated from the CO_2 gas stream are fed into the hydrator where they react with liquid water to produce $\text{Ca}(\text{OH})_2$. The obtained $\text{Ca}(\text{OH})_2$ is stored in a silo for use during the next period of the NGCC backup power block operation. The heat available from the gas and solid streams leaving the oxy-calciner can be recovered for power generation in a small steam cycle, as in base-load operated CaL systems, or used to preheat the CaO and O_2 streams to minimize the energy demand of the oxy-calciner block, as presented subsequently.

2.1. Reference natural gas combined cycle power plant

An NGCC based on a single-cycle gas turbine was used as the reference backup system. The NGCC power plant, including the gas turbine and HRSG, was modeled using the Aspen Hysys® software to solve the mass and heat balances in the steady-state mode during the operating periods, marked by step changes. The transient periods during the start-up and shut-down processes of the backup power plant were not considered in this study.

This system is considered to operate with a CF of 0.1 during a maximum period of 5 h. The basic scheme of this power plant is shown in Fig. 2. The main operational parameters were selected based on the data available in the literature as inputs to the process model.^{34,35} The gas turbine produces 70 MW_e and is assumed to operate at a compression pressure ratio of $18:1$.³³ Moreover, it has a single efficiency of 36.8% and an isentropic efficiency of 90%.³⁶ To simplify this example, it is assumed that the fuel is composed of CH_4 with a lower heating value of 50 MJ kg^{-1} . During operation, a fuel flow of 3.8 kg s^{-1} is burned producing 166.7 kg s^{-1} of flue gas with a composition of 4%_v CO_2 , 8%_v H_2O , 12.2%_v O_2 and the rest is N_2 . The flue gas exits the turbine at 625°C and 1.04 bar. A pressure loss on the hot side of the HRSG of 2.8% is assumed.³⁷ The heat available from the flue gas is recovered in an HRSG, which includes a steam cycle operated with live steam at 565°C and 166.5 bar. The main conditions of this cycle are shown in Fig. 3.^{34,35} This allows an additional power of 40.8 MW_e to be produced, which results in a combined cycle efficiency of 58.3% (η_{Ref} , being calculated as the ratio between the electrical power output, 110.8 MW_e , and the thermal power input from the fuel, $190 \text{ MW}_{\text{th}}$).

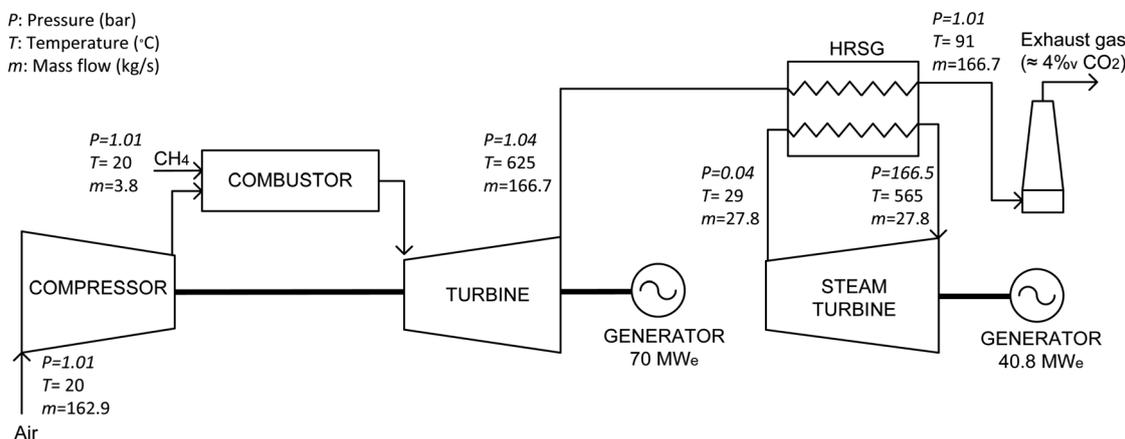


Fig. 2 Simplified schematic of the reference NGCC. Reported pressure (P in bar), temperature (T in $^\circ\text{C}$), and mass flow (m in kg s^{-1}).

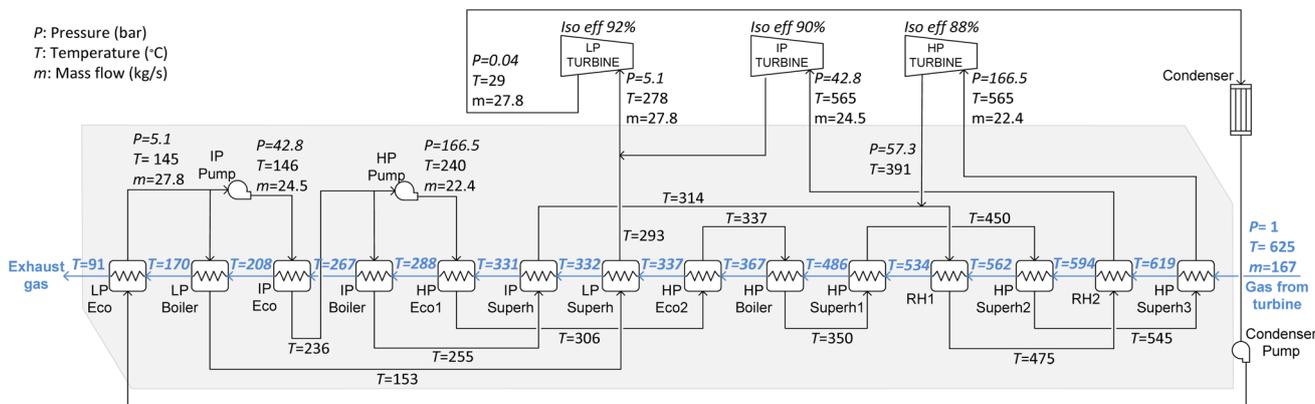


Fig. 3 Reference HRSG. Reported pressure (P in bar), temperature (T in $^\circ\text{C}$), and mass flow (m in kg s^{-1}) corresponding to the reference NGCC presented in Fig. 2. "Iso eff" refers to the isentropic efficiency assumed for the turbines.



3. Results and discussion

In this section, a case study is analyzed to demonstrate the operation and performance of the process shown in Fig. 1. As for the NGCC power plant, the carbonator, oxy-calcliner, and hydrator reactors were modeled in Aspen Hysys®. Mass and heat balances were solved in the steady-state mode during the operating periods. For the power plant with CO₂ capture, the start-up time was considered similar to those of standard NGCCs³⁸ because carbonator preheating is not required to achieve the reaction conditions.

3.1. Integration of the backup CO₂ capture process

Fig. 4 and 5 show the integration of the CO₂ capture system and regeneration of the sorbent in the backup power plant. As presented above, the carbonator is located at the exit of the gas turbine, and the decarbonized flue gas is fed into the HRSG (Fig. 4) to capture 90% of the CO₂ produced in the NGCC power plant. The data for the gas and solid streams of the integrated process are listed in Table 1. For simplicity, it was assumed that an ideal separation of the solids and gases occurred at the exit of the carbonator, oxy-calcliner, and hydrator reactors by using high efficiency cyclones, aided by the agglomeration tendency of the very fine powder used. In a non-ideal case, a make-up flow of limestone should be fed into the calciner to maintain the inventory of sorbent and compensate for solid losses.

In the integration scheme shown in Fig. 4, the carbonator induces a certain pressure drop in the system, affecting the conditions of the flue gas and thus the turbine efficiency. A conservative pressure drop in the carbonator reactor of 10% was assumed.^{39,40} This increases the outlet turbine pressure up to 1.16 bar, resulting in an isentropic temperature of 652 °C at a heat capacity ratio of 1.37. Consequently, the temperature of the flue gas leaving the turbine is approximately 650 °C. As

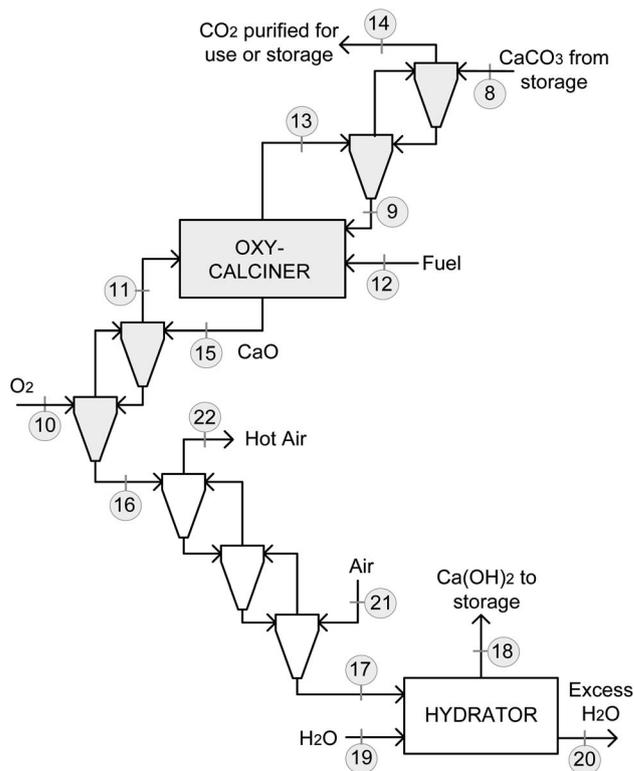


Fig. 5 Sorbent regeneration proposed for the backup CO₂ capture system including the oxy-calcination of the carbonated sorbent (in grey) and the hydration of the CaO (in white).

a result, the turbine power generation is reduced from 70 MW_e (as in the configuration of Fig. 2) to 65 MW_e. Under these new operating conditions, a single efficiency of 34.2% is obtained for the gas turbine shown in Fig. 4.

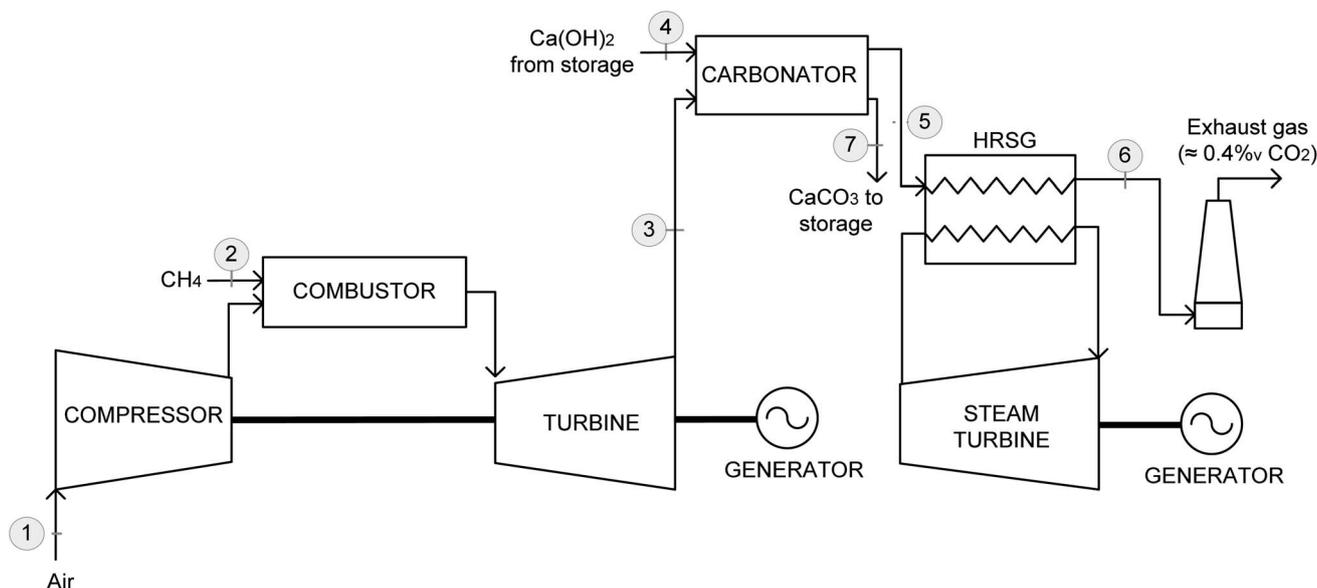


Fig. 4 Integration proposed for the CO₂ capture system in the backup NGCC power plant.



Table 1 Stream specifications of the CO₂ capture system integrated in the reference NGCC with CF = 0.1 (see Fig. 4 and 5)

No. (Fig. 4 and 5)	Description	Temperature (°C)	Mass flow (kg s ⁻¹)	Composition (% _{wt} for solids and % _v for gases/liquids)
1	Air to gas turbine	20	162.9	21% _v O ₂ , 79% _v N ₂
2	Fuel to combustor	20	3.8	100% _v CH ₄
3	Gas from turbine to carbonator	650	166.7	12.2% _v O ₂ , 75.8% _v N ₂ , 4.0% _v CO ₂ , 8.0% _v H ₂ O
4	Ca(OH) ₂ from storage to carbonator	100	22.4	100% _{wt} Ca(OH) ₂
5	Gas from carbonator to HRSG	602	162.8	12.0% _v O ₂ , 74.7% _v N ₂ , 0.4% _v CO ₂ , 12.9% _v H ₂ O
6	Gas outlet HRSG	95		
7	CaCO ₃ from carbonator to storage	602	26.2	80.6% _{wt} CaCO ₃ , 19.4% _{wt} CaO
8	CaCO ₃ from storage to oxy-calciner	602	2.6	
9	Preheated CaCO ₃ to oxy-calciner	765		
10	O ₂ to oxy-calciner	20	0.4	100% _v O ₂
11	Preheated O ₂ to oxy-calciner	875		
12	Fuel to oxy-calciner	20	0.1	100% _v CH ₄
13	CO ₂ from oxy-calciner	920	1.4	3.4% _v O ₂ , 68.5% _v CO ₂ , 28.1% _v H ₂ O
14	CO ₂ purified to use or storage	663		
15	CaO from oxy-calciner	920	1.7	100% _{wt} CaO
16	CaO to hydrator block	709		
17	CaO to hydrator	80		
18	Ca(OH) ₂ to storage	100	2.2	100% _{wt} Ca(OH) ₂
19	H ₂ O(l) to hydrator	20	1.3	100% _v H ₂ O
20	H ₂ O excess exit hydrator	100	0.7	
21	Air for cooling CaO	20	2.6	21.0% _v O ₂ , 79.0% _v N ₂
22	Hot air after cooling CaO	376		

Owing to the lower carbonation enthalpy of Ca(OH)₂, the heat balance in the adiabatic carbonator is governed by the temperature of the gas and solids entering the reactor.²⁸ The possibility of integrating residual heat from the power plant (*i.e.*, that is contained in the exhausted flue gas from the HRSG) to preheat the sorbent before entering the carbonator is limited. Therefore, the temperature at which the sorbent enters the carbonator will be driven by the Ca(OH)₂ storage conditions and, therefore, by the CaO hydration conditions. In the typical Ca(OH)₂ production processes the hydrator consists of, for example, rotating paddles which agitate the lime in the presence of water.³⁰ The strong exothermic reaction between water and CaO takes place in these reactors at an average temperature of approximately 100 °C, with the reaction heat (+104 kJ mol⁻¹ of CaO) moderated by the addition of excess water (typically at a water-to-lime ratio in the range of 2 : 1 to 3 : 1 (ref. 41)). Based on this, Ca(OH)₂ solids are stored and fed to the carbonator reactor at 100 °C. This temperature also prevents the dehydration of the bulk of the solids as the equilibrium partial steam pressure is just 7×10^{-8} bar.⁴²

When feeding the gas and solids to the carbonator at temperatures of 650 °C and 100 °C respectively, the temperature at the exit of the carbonator reactor was calculated as 602 °C. At such temperature the molar conversion of Ca to CaCO₃ can be up to 0.7 for a gas–solid contact time of just 4 s.²⁸ Therefore, for a capture efficiency of 90%, a Ca(OH)₂ flow of 22.4 kg s⁻¹ is required. After the carbonation reaction the gas and solid streams are separated. Due to the moderate temperature of such streams, the most favorable option to separate the solids from the gas before entering the HRSG is high efficiency cyclones as mentioned above. The tendency of solids to agglomerate also facilitates their separation from the gas phase

by enhancing the cyclone efficiency.²³ If required, a filter or electrostatic precipitator could be as well added before the stack after the HRSG, to further recover possible particles dragged by the gas flow, taking into account that contents about 30 g m⁻³ are common in heat recovery systems.⁴³ Then, the carbonated solids are stored and the decarbonized flue gas (162.8 kg s⁻¹) is transferred to the HRSG for heat recovery. An integration scheme similar to that in the reference power plant (Fig. 3) was used to recover heat from the flue gas, in this case at 602 °C. This scheme allows the flue gas to cool down to a temperature of 95 °C before being exhausted, producing an additional power of 38.5 MW_e in the steam cycle. During the power-production periods a total of 103.5 MW_e is generated in the backup NGCC power plant with CO₂ capture. When compared with the reference NGCC without capture, the combined cycle efficiency is reduced to 54.5% (the reference being 58.3%).

As shown in Fig. 4, the CaCO₃-rich solids leaving the carbonator are directly transferred to the CaCO₃ storage at the outlet carbonator temperature. This will help to minimize the energy consumption in the oxy-calciner. For applications aimed at long-term storage and/or with larger sorbent requirements, the carbonated sorbent can be cooled down to facilitate storage operations. In such a case, the heat available from the solids leaving the carbonator can be integrated into the steam cycle of the HRSG to minimize the energy penalties.

To operate the backup power plant for a maximum of 5 h, the total amount of stored Ca(OH)₂ is 403 ton (and 472 ton of CaCO₃-rich solids). To achieve this requirement, a continuous flow of CaCO₃-rich solids (2.6 kg s⁻¹, an order of magnitude smaller than the equivalent molar flow of Ca(OH)₂ fed into the carbonator) is fed from the CaCO₃ silo into the oxy-calciner (Fig. 5). For simplicity, this reactor uses the same fuel as that



in the NGCC power plant and is burnt with O₂. The oxygen used in the calciner is assumed to be produced in an air separation unit. However, in the future, low-cost hydrogen produced by water electrolysis could be available extensively, and the oxygen obtained as a sub-product may be used to minimize the energy penalty associated with oxy-calcination. Moreover, alternative fuels, such as biomass (to achieve negative emissions) or electrolytic green-H₂ obtained from renewable electricity (to electrify the CO₂ capture process), may be used in the oxy-calciner, especially considering its reduced thermal capacity, as discussed below.

In standard CaL systems, the heat available in the CO₂-rich flue gas and CaO solids leaving the oxy-calciner is used to produce additional power in a dedicated steam cycle. However, because of the low thermal capacity of the oxy-calciner in this application, the heat available is used to preheat the carbonated sorbent coming from the CaCO₃ storage and the oxygen fed into the calciner. The integration scheme for preheating these streams is shown in Fig. 5. Thus, the CO₂-rich flue gas is contacted with the carbonated solids in a 2-step cyclonic preheater, similar to those used in cement plants to increase the temperature of the raw meal. Similarly, oxygen fed into the calciner is preheated using CaO solids in a 2-step cyclonic preheater. The calciner is operated at a temperature of 920 °C to ensure complete calcination of the sorbent. Therefore, the integration scheme shown in Fig. 5 allows the preheating of the carbonated solids and oxygen up to temperatures of 765 and 875 °C, respectively, before entering the calciner. Consequently, a thermal input into the oxy-calciner of 4.4 MW_{th} is calculated, which is produced by combusting 0.1 kg s⁻¹ of CH₄ with 0.4 kg s⁻¹ of O₂. The CO₂-rich flue gas with a flow of 1.4 kg s⁻¹ is separated from the calcined solids and then transferred to a compression and purification unit (not shown in Fig. 5 for simplicity). To reduce the energy demand during calcination or prevent the potential problems associated with the preheating steps for pure O₂ there are additional possibilities for thermal integration. For example, Robin *et al.*⁴⁴ developed a similar oxy-fired calciner in which hot air produced during the cooling of CaO was used to preheat part of the CaCO₃ feed to the calciner. However, it is noteworthy that in the system here proposed, the energy cost can be very low during the regeneration stages. Therefore, intensive integration efforts to achieve adequate economics may not be required.

As presented above, the CaO produced during calcination is used to obtain Ca(OH)₂ *via* the standard hydration method. In the case of the proposed scheme shown in Fig. 5, the flow of hot CaO solids must be cooled before being fed into the hydrator. This is achieved by contacting the solids with an air flow of 2.6 kg s⁻¹ at 20 °C in a 3-step cyclonic cooler, which reduces the temperature of CaO to 80 °C. In the hydrator, liquid water is added in excess of 2.3 relative to the stoichiometric value to control the temperature and operate the hydrator at a typical temperature of 100 °C.^{30,41} This results in a water flow consumption of 1.3 kg s⁻¹ and an excess of 0.7 kg s⁻¹, which is discharged as steam into the atmosphere. After hydration, the Ca(OH)₂ flow produced (2.2 kg s⁻¹) is transferred to the storage silo.

To estimate the energy penalty associated with sorbent regeneration, specific power consumptions of 200 kW h_e per tO₂ and 120 kW h_e per tCO₂ were assumed for the air separation and CO₂ compression and purification units, respectively.⁴⁵ Additionally, a power consumption of 0.15 kW_e relative to the kW_{th} fed into the calciner was considered for the auxiliaries used in the sorbent regeneration block.⁴⁶ Based on these assumptions, a global efficiency (η_{Global}) of 38.2% was calculated using eqn (1), where $P_{\text{th, CC}}$ and $P_{\text{th, oxy}}$ are the thermal inputs to the gas turbine and oxy-calciner blocks (190 and 4.4 MW_{th}, respectively), $P_{\text{e, CC}}$ is the electric power output from the NGCC in Fig. 4 (103.5 MW_e), and $P_{\text{e, O}_2}$, $P_{\text{e, CO}_2}$, and $P_{\text{e, aux}}$ are the electrical consumption (1.4 MW_e) for the air separation, CO₂ compression and purification, and auxiliaries, respectively.

$$\eta_{\text{Global}} = \frac{P_{\text{e, CC}} \times \text{CF} - (P_{\text{e, O}_2} + P_{\text{e, CO}_2} + P_{\text{e, aux}})}{P_{\text{th, CC}} \times \text{CF} + P_{\text{th, oxy}}} \quad (1)$$

4. Cost analysis

A basic economic analysis was performed to estimate the cost of CO₂ avoided (AC). A NGCC power plant with an emission factor of 336 kg_{CO₂} kW⁻¹ h_e⁻¹ was used as the reference system, and the AC was calculated using eqn (2):

$$\text{AC} = \frac{\Delta\text{COE}_{\text{Capture}}}{(\text{CO}_2 \text{ per kW per h}_e)_{\text{Ref NGCC}} - (\text{CO}_2 \text{ per kW per h}_e)_{\text{Capture}}} \quad (2)$$

where $\Delta\text{COE}_{\text{Capture}}$ is the increment in the cost of electricity owing to the CO₂ capture process, and $(\text{CO}_2 \text{ per kW per h}_e)_{\text{Ref NGCC}}$ and $(\text{CO}_2 \text{ per kW per h}_e)_{\text{Capture}}$ are the CO₂ emission factors for the reference NGCC and NGCC with CO₂ capture, respectively. To simplify the analysis, the same fixed and variable operating costs were considered for both systems. $\Delta\text{COE}_{\text{Capture}}$ was estimated using the following equation:

$$\Delta\text{COE}_{\text{Capture}} = \frac{\Delta\text{TCR} \times \text{FCF}}{\text{CF} \times 8760} + \text{FC} \left(\frac{1}{\eta_{\text{Global}}} - \frac{1}{\eta_{\text{Ref}}} \right) + \text{H}_2\text{O}_{\text{Cost}} \quad (3)$$

where ΔTCR is the total capital requirement related to the new elements needed for the CO₂ capture, FCF is the fixed charge factor, FC is the fuel cost, η_{Global} and η_{Ref} are the efficiencies of the NGCC with CO₂ capture (eqn (1)) and the reference NGCC (Fig. 2), respectively, and $\text{H}_2\text{O}_{\text{Cost}}$ is the water cost. Table 2 lists the main data used in the cost analysis. Six elements were considered to be the main contributors to the capital requirements of the CO₂ capture process, including the adiabatic carbonator, oxy-calciner, hydrator, sorbent storage system, air separation unit (ASU), and CO₂ compression and purification unit (CPU). The reference costs of these elements were obtained from data available in the literature.^{13,47–50} ΔTCR was calculated per power unit by estimating the specific cost of each element based on the cost of similar commercial elements as in previous works.⁸ The power fractions compared to the total power input to the NGCC (operated at CF = 0.1) and oxy-calciner/hydrator



Table 2 Main values of NGCC and Ca(OH)₂-based CaL for the cost analysis of the reference case presented in Table 1

Parameter	Units	NGCC + CaO/Ca(OH) ₂ /CaCO ₃ CaL
Increment of total capital requirements, ΔTCR	\$ per kW _{th} (\$ per kW _e)	94 (245)
Fraction of power to NGCC, f_{NGCC}	—	0.81
Fraction of power to oxy-calcliner/hydrator, f_{Oxy}	—	0.19
Fixed charge factor, FCF	Per year	0.1
Fuel cost, FC	\$ per GJ	10
Water cost, H ₂ O _{Cost}	\$ per m ³	1.5
Global efficiency, η_{Global}	kW _e kW _{th} ⁻¹	0.382
Reference NGCC efficiency, η_{Ref}	kW _e kW _{th} ⁻¹	0.583
Storage time, $t_{Storage}$	h	5
CO ₂ emission factor for the reference NGCC, (CO ₂ per kW per h _e) _{Ref NGCC}	kg CO ₂ per MW per h _e	336
CO ₂ emission factor, (CO ₂ per kW per h _e) _{Capture}	kg CO ₂ per MW per h _e	36
$\Delta COE_{Capture}$ (CF = 0.1)	\$ per kW per h _e	0.061
AC (CF = 0.1)	\$ per tCO ₂	204

blocks (f_{NGCC} and f_{Oxy} , respectively) are used in eqn (4) to consider the contribution of each element to the entire process.

$$\Delta TCR = (TCR_{Carbo} + TCR_{CPU}CF + 2TCR_{Storage}t_{Storage})f_{NGCC} + (TCR_{Oxy} + TCR_{Hyd} + TCR_{ASU})f_{Oxy} \quad (4)$$

The cost of the oxy-calcliner and gas/solid preheating system (TCR_{Oxy}) was assumed to be 125 \$ per kW_{th}, which is equivalent to a cement plant pre-calcliner with cyclone suspension preheaters, where approximately 90% of the cost is attributed to the preheater system.⁵⁰ The cost associated with the adiabatic carbonator (that is, a refractory bed) was considered to be identical to that of a pre-calcliner ($TCR_{Carbo} = 15$ \$ per kW_{th}). The cost associated with the Ca(OH)₂ and CaCO₃ storage silos and their corresponding handling equipment was calculated based on a limestone cost of 10 \$ per t (ref. 51) and the silos were dimensioned to operate for a maximum NGCC operation period ($t_{Storage}$) of 5 h, resulting in a $TCR_{Storage}$ of 0.2 \$ per kW per h_{th}. The costs associated with the CPU and ASU (TCR_{CPU} and TCR_{ASU}) were 80 and 110 \$ per kW_{th}, respectively.⁴⁵ Finally, the cost of CaO hydration (TCR_{Hyd}) was estimated based on the cost of the cyclone suspension preheaters (115 \$ per kW_{th})⁵⁰ that are required to cool down the calcined solids plus the cost of the hydrator (40 \$ per kW_{th}),⁵² resulting in a TCR_{Hyd} of 155 \$ per kW_{th}.

As listed in Table 2, the calculated increment in the cost of electricity is 0.061 \$ per kW per h_e, which is a reasonable value considering the extremely low capacity factor assumed (CF = 0.1). This results in a cost of CO₂ avoided of 204 \$ per tCO₂ according to eqn (2). The flexible CO₂ capture system evaluated in this study is a feasible option for retrofitting amortized natural gas power plants in future scenarios with high carbon prices and a large portion of renewables. Although the carbon prices required to make these CO₂ capture systems economically feasible exceed the current prices, this technology may serve as a complementary system for low-carbon power mixes.⁵³ Moreover, it may be considered a reasonable compromise to “close the carbon loop” in power-to-gas-to-power systems involving the manufacture of synthetic fuels from CO₂, which

otherwise leak CO₂ into the atmosphere during the gas-to-power step.

5. Conclusions

CaL systems using Ca(OH)₂ as a sorbent can be integrated into NGCC power plants operating at an extremely low capacity factor, benefiting from the favorable kinetics and carrying capacities of the sorbent. For this purpose, intermediate storage of the solids was used to decouple CO₂ capture and sorbent regeneration. This reduces the capacity of elements related to sorbent regeneration and the investment cost while minimizing the energy penalty during power-production periods.

A case for an NGCC power plant with a thermal input of 190 MW_{th} and operating at a CF of 0.1 was evaluated. The CO₂ capture process was integrated with minor modifications to the operating conditions of the gas turbine and heat-recovery steam generator. The power delivered by the NGCC power plant was reduced by 6.6% relative to the conventional system without CO₂ capture during power-production periods. The thermal input of the oxy-calcliner required to regenerate the sorbent was just 4.4 MW_{th} resulting in a global efficiency of 38.2%. Storage capacities of 403 and 472 tons of Ca(OH)₂ and CaCO₃-rich solids, respectively, were required to operate the gas turbine for maximum periods of 5 h. To minimize thermal input into the calcliner, the carbonated sorbent was stored at the carbonator outlet temperature (602 °C). A basic economic analysis was performed, indicating a cost of CO₂ avoided of approximately 200 \$ per tCO₂. This suggests that the proposed system is a feasible option for capturing CO₂ from natural gas power plants in future scenarios with high carbon prices and a large share of renewables in the global energy mix, or for closing the carbon loop in emerging power-to-gas-to-power energy storage systems.

Conflicts of interest

There are no conflicts of interest to declare.



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References

- IPCC, *Climate change 2022 – mitigation of climate change, summary for policymakers*, Working Group III contribution to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change, 2022.
- IEA, *European Union 2020: energy policy review*, International Energy Agency, Paris, France, 2020.
- I. Tsiropoulos, W. Nijs, D. Tarvydas and P. Ruiz Castello, *Towards net-zero emissions in the EU energy system by 2050 – insights from scenarios in line with the 2030 and 2050 ambitions of the European Green Deal*, EUR 29981 EN, Luxembourg, 2020.
- M. A. Gonzalez-Salazar, T. Kirsten and L. Prchlik, *Renewable Sustainable Energy Rev.*, 2018, **82**, 1497–1513.
- IRENA, *Flexibility in conventional power plants: innovation landscape brief*, International Renewable Energy Agency, Abu Dhabi, 2019.
- A. S. Brouwer, M. van den Broek, A. Seebregts and A. Faaij, *Appl. Energy*, 2015, **156**, 107–128.
- A. M. Abdilahi, M. W. Mustafa, S. Y. Abujarad and M. Mustapha, *Renewable Sustainable Energy Rev.*, 2018, **81**, 3101–3110.
- Y. A. Criado, B. Arias and J. C. Abanades, *Energy Environ. Sci.*, 2017, **10**, 1994–2004.
- M. Astolfi, E. De Lena and M. C. Romano, *Int. J. Greenhouse Gas Control*, 2019, **83**, 140–155.
- M. Astolfi, E. De Lena, F. Casella and M. C. Romano, *Appl. Therm. Eng.*, 2021, **194**, 117048.
- B. Arias, Y. A. Criado and J. C. Abanades, *ACS Omega*, 2020, **5**, 4844–4852.
- J. C. Abanades, B. Arias, A. Lyngfelt, T. Mattisson, D. E. Wiley, H. Li, M. T. Ho, E. Mangano and S. Brandani, *Int. J. Greenhouse Gas Control*, 2015, **40**, 126–166.
- NETL, *Cost and performance baseline for fossil energy plants volume 1: bituminous coal and natural gas to electricity*, National Energy Technology Laboratory, United States, 2019.
- A. W. D. Hills, *Inst. Min. Metall.*, 1967, **76**, C241–C245.
- Y. Hu and H. Ahn, *Appl. Energy*, 2017, **187**, 480–488.
- M. Erans, D. Hanak, J. Mir, E. Anthony and V. Manovic, *Therm. Sci.*, 2016, **20**, 59–67.
- C. Fu, S. Roussanaly, K. Jordal and R. Anantharaman, *Front. Chem. Eng.*, 2021, **2**, 28.
- D. Berstad, R. Anantharaman, R. Blom, K. Jordal and B. Arstad, *Int. J. Greenhouse Gas Control*, 2014, **24**, 43–53.
- Y. A. Criado, B. Arias and J. C. Abanades, *Ind. Eng. Chem. Res.*, 2018, **57**, 12595–12599.
- Z. Li, F. Fang, X. Tang and N. Cai, *Energy Fuels*, 2012, **26**, 2473–2482.
- V. Manovic and E. J. Anthony, *Ind. Eng. Chem. Res.*, 2010, **49**, 9105–9110.
- S. K. Bhatia and D. D. Perlmutter, *AIChE J.*, 1983, **29**, 79–86.
- N. Phalak, W. Wang and L.-S. Fan, *Chem. Eng. Technol.*, 2013, **36**, 1451–1459.
- L. S. Fan, S. Ramkumar, W. Wang and R. Statnick, *US Pat.*, US 8512611 B2, 2013.
- W. Wang, S. Ramkumar, D. Wong and L. S. Fan, *Fuel*, 2012, **92**, 94–106.
- F. Zeman, *Int. J. Greenhouse Gas Control*, 2008, **2**, 203–209.
- B. Arias, Y. A. Criado, B. Pañeda and J. C. Abanades, *Ind. Eng. Chem. Res.*, 2022, **61**, 3272–3277.
- Y. A. Criado and B. Arias, *ACS Omega*, 2022, **7**, 28093–28100.
- A. M. Carpenter, *Low water FGD technologies*, IEA Clean Coal Centre, 2012.
- F. Schorcht, I. Kourti, B. M. Scalet, S. Roudier and L. Delgado Sancho, *Best Available Techniques (BAT) reference document for the production of cement, lime and magnesium oxide*, Publications Office of the European Union, Luxembourg, 2013.
- W.-C. Chen, S. Ouyang, C.-M. Huang, C.-H. Shen and H.-W. Hsu, *US Pat.*, US 9610537 B2, 2017.
- J. C. Abanades, B. Arias and Y. A. Criado, EP20383113, European Patent Office, 2020.
- Siemens, *Reliable gas turbines*, <https://www.siemens-energy.com/global/en/offers/power-generation/gas-turbines.html>.
- DOE/NETL, *Cost and performance baseline for fossil energy plants volume 1a: bituminous coal (PC) and natural gas to electricity, Revision 3.*, US Department of Energy, National Energy Technology Laboratory, 2015.
- IEAGHG, *CO₂ capture at gas fired power plants*, 2012/8, International Energy Agency Greenhouse Gas R&D Programme, 2012.
- M. M. Rahman, T. K. Ibrahim and A. N. Abdalla, *Int. J. Phys. Sci.*, 2011, **6**, 3539–3550.
- S. Dybe, M. Bartlett, J. Pålsson and P. Stathopoulos, *Sustainability*, 2021, **13**, 651.
- DOE/NETL, *Impact of load following on power plant cost and performance: literature review and industry interviews*, US Department of Energy, National Energy Technology Laboratory, 2012.
- M. Spinelli, I. Martínez, E. De Lena, G. Cinti, M. Hornberger, R. Spörl, J. C. Abanades, S. Becker, R. Mathai, K. Fleiger, V. Hoenig, M. Gatti, R. Scaccabarozzi, S. Campanari, S. Consonni and M. C. Romano, *Energy Procedia*, 2017, **114**, 6206–6214.
- E. De Lena, M. Spinelli, M. Gatti, R. Scaccabarozzi, S. Campanari, S. Consonni, G. Cinti and M. C. Romano, *Int. J. Greenhouse Gas Control*, 2019, **82**, 244–260.
- R. S. Boynton, *Chemistry and technology of lime and limestone*, John Wiley & Sons, New York, 2nd edn, 1980.
- I. Barin, *Thermochemical data of pure substances*, VCH Verlagsgesellschaft Weinheim, Germany, 1989.



- 43 M. Pronobis, *Environmentally oriented modernization of power boilers*, 1st edn, 2020.
- 44 C. Robin, C. Pierre-Olivier, S. B. Guthrie and J. C. Abanades, WO2022/049137A1, World Intellectual Property Organization, 2022.
- 45 A. Darde, R. Prabhakar, J.-P. Tranier and N. Perrin, *Energy Procedia*, 2009, **1**, 527–534.
- 46 L. M. Romeo, J. C. Abanades, J. M. Escosa, J. Paño, A. Giménez, A. Sánchez-Biezma and J. C. Ballesteros, *Energy Convers. Manage.*, 2008, **49**, 2809–2814.
- 47 NREL, *Cost and performance data for power generation technologies*, National Renewable Energy Laboratory, USA, 2012.
- 48 IEA-ETSAP, *Technology brief E02: gas-fired power*, International Energy Agency – Energy Technology Systems Analysis Programme, Paris, France, 2010.
- 49 G. Guandalini, M. C. Romano, M. Ho, D. Wiley, E. S. Rubin and J. C. Abanades, *Int. J. Greenhouse Gas Control*, 2019, **84**, 219–231.
- 50 IEAGHG, *CO₂ capture in the cement industry*, International Energy Agency Greenhouse Gas R&D Programme, 2008.
- 51 USGS, *Crushed stone statistics and information*, <https://www.usgs.gov/centers/nmic/crushed-stone-statistics-and-information>.
- 52 P. Renforth, B. G. Jenkins and T. Kruger, *Energy*, 2013, **60**, 442–452.
- 53 IEA, *Projected costs of generating electricity 2020*, International Energy Agency, Paris, France, 2020.

