ACS OMEGA

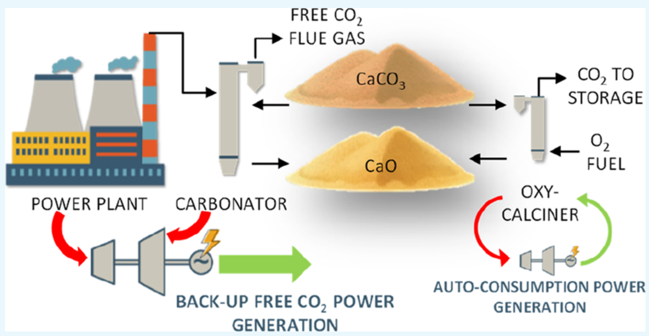
http://pubs.acs.org/journal/acsodf Article

Thermal Integration of a Flexible Calcium Looping CO_2 Capture System in an Existing Back-Up Coal Power Plant

Borja Arias, Yolanda A. Criado,* and J. Carlos Abanades

Cite This: ACS Omega 2020, 5, 4844−4852 Read Online

ABSTRACT: The CO_2 capture from back-up power plants by making use of calcium looping systems combined with large piles of Ca-solids has been studied in this work. A flexible CO_2 capture system based on a concept described in a previous work has been integrated into an existing power plant by including a small oxy-fired calciner (that represents just 8% of the total thermal capacity) to steadily regenerate the sorbent and a carbonator reactor following the back-up power plant operation periods to capture 90% of the CO_2 as $CaCO_3$ and two large piles of rich CaO and $CaCO_3$ solids stored at modest temperatures. When the back-up plant enters into operation, the calcined solids are brought into contact with the flue gases in the carbonator reactor; meanwhile, the oxy-calciner operates continuously at a steady state. In order to improve the flexibility of the CO_2 capture system and to minimize the increase of CO_2 capture costs associated with the additional new equipment used only during the brief back-up periods, we propose using the steam cycle of the existing power plant to recover a large fraction of the heat available from the streams leaving the carbonator. This makes it possible to maintain the electrical power output but reducing the thermal input to the power plant by 12% and thus the size of the associated CO_2 capture equipment. To generate the auxiliary power required for the oxy-calciner block, a small steam cycle is designed by integrating the waste heat from the streams leaving this reactor. By solving the mass and heat balances and proposing a feasible thermal integration scheme by using Aspen Hysys, it has been calculated that the CO_2 emitted by long-amortized power plants operated as back-up can be captured with a net efficiency of 28%.



1. INTRODUCTION

Renewable power is expected to be the dominant energy source in future energy networks, with shares of the total electricity demand of between 75 and 80% by 2060.[1,2] Back-up combustion and/or energy storage systems will be required to maintain the balance between supply and demand in such systems.[2,3] Existing amortized coal power plants operated as back-up could be favored in such future electricity grids by market mechanisms, as they use a relatively low-cost fuel and can be largely amortized.[3−6]

However, the decarbonization of these combustion back-up power plants by means of CO_2 capture and storage (CCS) technologies will be needed to accomplish the aggressive CO_2 emission reduction targets established for the next few decades.[7] CCS systems have a limited flexibility to cope with the fluctuations in the flue gas loads and, what is more, their high investment costs seriously limit their applicability at low capacity factors (CFs).[8−14] A number of solutions have been proposed in the literature to increase the flexibility of the CO_2 capture systems, most of which involve the storage of different functional materials. The storage of a fraction of the rich solvent has been studied in post-combustion amine-based CO_2 capture systems[14−16] to reduce the consumption of power in the regeneration and CO_2 compression units (CPU) during the periods of peak power demand, so that these operations can be postponed to when there is less demand. The storage of O_2 in cryogenic tanks during low power demand periods while operating the air separation unit (ASU) in base mode has been proposed for oxy-combustion systems.[17−19] Similarly, the storage of H_2 in pre-combustion CO_2 capture systems has been analyzed to decouple the generation of power from H_2 production.[20,21] However, these approaches are aimed at achieving short-term flexibility (i.e., ranging from minutes to hours) to cover short peaks characterized by a fast response. In the case of seasonal back-up (i.e., operating only a few weeks per year), such CO_2 systems will be penalized due to the required large-capacity storage of costly materials (such as amines) or due to the use of large-scale storage equipment (i.e., for cryogenic O_2 or pressurized H_2).

Received: October 23, 2019
Accepted: February 20, 2020
Published: March 3, 2020

https://dx.doi.org/10.1021/acsomega.9b03552
ACS Omega 2020, 5, 4844−4852

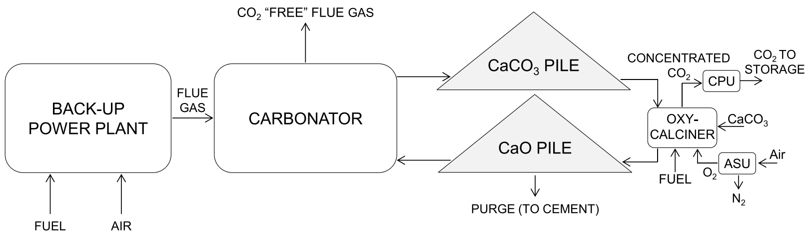


Figure 1. Schematic representation of the highly flexible back-up fossil power plant with CO_2 capture by CaL including $CaO/CaCO_3$ storage (FlexiCaL).

A CO_2 capture process to improve the flexibility of calcium looping (CaL) technology has been recently proposed in order to take advantage of the low specific cost of the solids required for large-scale storage, that is, CaO and $CaCO_3$ derived from crushed limestone.[22] CaL technology has advanced rapidly in the last decade and it has been demonstrated at TRL6 in several pilot plants.[23−28] The similarity of its core components, the circulating fluidized bed (CFB) carbonator and calciner reactors, with existing CFB boiler technology has led to several testing and modeling studies,[29−33] process simulation, and integration[34−38] as well as cost analyses[33,39−41] in a wide range of configurations. Despite the progress achieved in the CaL technology, the flexibility of CaL systems against flue gas load changes has received relatively low attention until recently.[42−44] Some authors have also simulated CaL-based energy storage systems for CCS[45,46] and solar power applications,[47] respectively, by making use of the thermal and/or thermochemical energy contained in the streams and/or reactions of the CaL system.

In the present work, we investigate the thermal integration of a particular reference flexible CaL case that could be used to extend the life of existing coal-fired power plants operated as back-up power systems. The main goal for this system is to minimize the cost of the carbon-free back-up power service by reducing the capital investment associated with the CO_2 capture. In addition, this process aims to moderate as much as possible energy penalties and to concentrate them in periods of low power demand. For this purpose, the use of the existing power plant steam cycle to integrate the heat available from the carbonation reaction has been studied in this work as a mean to reduce the cost of the CaL equipment, which is essential for its viability when operating under the low CFs expected in any decarbonized back-up power system.

2. PROCESS DESCRIPTION

The general scheme of the CO_2 capture system analyzed in this work (referred to as "FlexiCaL" from this point on) is presented in Figure 1. This process presents features in common with a conventional CaL configuration, such as the use of two CFB reactors, the carbonator and the calciner, but it also includes additional features to ensure the flexible operation of the CO_2 capture system, as was discussed in our previous work.[22]

As shown in Figure 1, one of the main characteristics of the FlexiCaL system is the use of two low-cost piles (or silos) of CaO- and $CaCO_3$-rich material (referred to as CaO and $CaCO_3$ piles for simplicity, although other minor components such as sulfates or ash may also be present). These piles could be dimensioned as to allow the complete decoupling of the carbonator and calciner operation modes. Thus, calcined solids from the CaO pile are fed directly into the carbonator to react with the CO_2 present in the flue gas when the back-up power plant enters into operation. Meanwhile, the carbonated solids leaving this reactor are stored in the $CaCO_3$ pile and the "free" CO_2 gas stream is released. The FlexiCaL process in Figure 1 aims to minimize the temperature of the piles in order to facilitate the handling and storage of the CaO and $CaCO_3$ materials. As shown below, different integration schemes can be used to achieve this objective, reducing the temperature of the solids in the piles to below 250 °C.

As a high-temperature solid looping system, typical calcium looping schemes are characterized by its ability to recover waste heat in a boiler, not only from the exothermic carbonation reaction that typically takes place at 650 °C[48] but also from the integration of the gas and/or solids streams leaving the carbonator and calciner reactors. Unlike most CaL schemes that use boiler-type carbonators, the carbonator reactor in the process depicted in Figure 1 is assumed to be an adiabatic reactor from which no heat is recovered for power production. However, a significant amount of thermal energy can be recovered from the gas and solids streams leaving the carbonator reactor to produce power. Because the process in Figure 1 only targets extremely low CFs, the use of an additional steam cycle linked to the gas and solids streams from the carbonator is ruled out in this work in an attempt to minimize waste of capital. Therefore, a new approach is adopted in this work to recover part of the energy from the carbonation using the steam cycle of the existing back-up power plant. The availability of such thermal capacity from the carbonation allows a certain reduction of the coal thermal input. This leads to a reduction in the flow of CO_2 produced in the power plant and, therefore, in the amount of sorbent needed in the carbonator. Different integration schemes can be adopted to incorporate both the thermal power from the power plant and the carbonation heat available into a single steam cycle. In standard CaL schemes, some of these options where investigated by Yang et al.[36] However and in order to minimize the modifications in the power plant steam cycle and, thus, the capital cost, we have considered only the use of the carbonation heat to preheat the water entering the boiler, as discussed in the following section.

3. RESULTS AND DISCUSSION

A reference case is proposed to illustrate the performance of the FlexiCaL system of Figure 1. The power plant, carbonator, and oxy-calciner, as well as the associated steam cycles have been modeled using Aspen Hysys to solve the mass and energy balances in steady-state mode; meanwhile, the nonsteady operations related with the switching on and off of the power plant and carbonator block for the back-up periods has been left outside the scope of this work. Relevant parameters and values for the reference case described below are summarized in Table 1 and the different major elements in Figure 1 are detailed below.

Table 1. Main Parameters for the Reference Case Studied in This Work

description	unit	value
net electrical power output, $P_{e,net}$	MW_e	350
power plant thermal capacity, $P_{th,power\ plant\ ref}$	MW_{th}	777
net power plant efficiency, $\eta_{power\ plant}$	%	45
CF		0.1
carbonation temperature, T_{carb}	°C	650
oxy-calcination temperature, T_{calc}	°C	910
average CO_2 carrying capacity, X_{ave}		0.35
CO_2 capture efficiency, E_{carb}		0.9
calcination efficiency, E_{calc}		1

As general considerations for the analysis in the following sections, it has been assumed that heat losses in the solid piles can be neglected considering their low surface-to-volume ratio, and in gas−solid heat-exchange operations taking place in cyclonic preheaters, the outlet stream temperatures are equalized and the heat exchange efficiency in the steam cycles is of 95%.

As in other CaL systems and as considered for the reference case here presented, an additional benefit of the FlexiCaL process in Figure 1 is its potential synergy with a large-scale CaO consumer such as a cement plant. As in typical CaL, a certain flow of fresh limestone (make-up flow, F_0) is fed into the calciner in order to compensate for the decay in the sorbent's CO_2 carrying capacity and also to purge the inserts from the inventory of solids (ashes and $CaSO_4$ formed in the oxy-calciner). In addition, the low CFs of the system in Figure 1 allows for very high activity materials in the solid storage piles when employing make-up flows of limestone that satisfy the requirements of a typical cement plant.

3.1. Reference Coal-Fired Power Plant. An existing coal-fired power plant providing a net electric power of 350 MW_e is considered to be the back-up system and the source of the flue gas fed into the carbonator. This power plant employs a supercritical steam cycle operating with live steam at 600 °C and 280 bar. Figure 2 shows a simplified scheme of the steam cycle of the existing power plant. The main operation conditions of the steam cycle have been adopted from the data available in the literature[49] and assuming that a 5% of the gross power output is consumed by the auxiliaries, resulting in a net power efficiency of 45% (defined as the ratio between the net electrical output and the thermal input to the power plant). As a back-up system, the power plant is assumed to run at full load when it enters into operation, but with a low CF of 0.1 averaged over 1 year. During the operation periods, a coal thermal input of 777 MW_{th} is fed into the power plant, producing a flue gas flow of 10.4 kmol/s at 140 °C with 15.3 % v of CO_2. This power plant is assumed to be equipped with a desulfurization unit and, therefore, no SO_2 is emitted with the flue gas.

3.2. Back-Up CO_2 Capture and Thermal Integration of the Carbonator Block. A CO_2 capture efficiency of 90% has been chosen as the target in the carbonator operating at a temperature of 650 °C. An average CO_2 carrying capacity (X_{ave}) of 0.35 has been assumed. This value has been taken by considering that the flow of fresh limestone to the oxy-calciner reactor (F_0) is continuous (even when the carbonator and hence the power plant are not operating). This results in a flow of CaO particles with a high activity accumulating in the CaO pile that only react with CO_2 when the power plant and thus the carbonator enter into operation in back-up mode. For the sake of simplicity, it is considered that there is sufficient gas−solid contact time in the carbonator reactor to allow a conversion of 80% with respect to the maximum conversion attainable by the solids (X_{ave}). This high level of conversion has been demonstrated to be feasible in several large-scale calcium

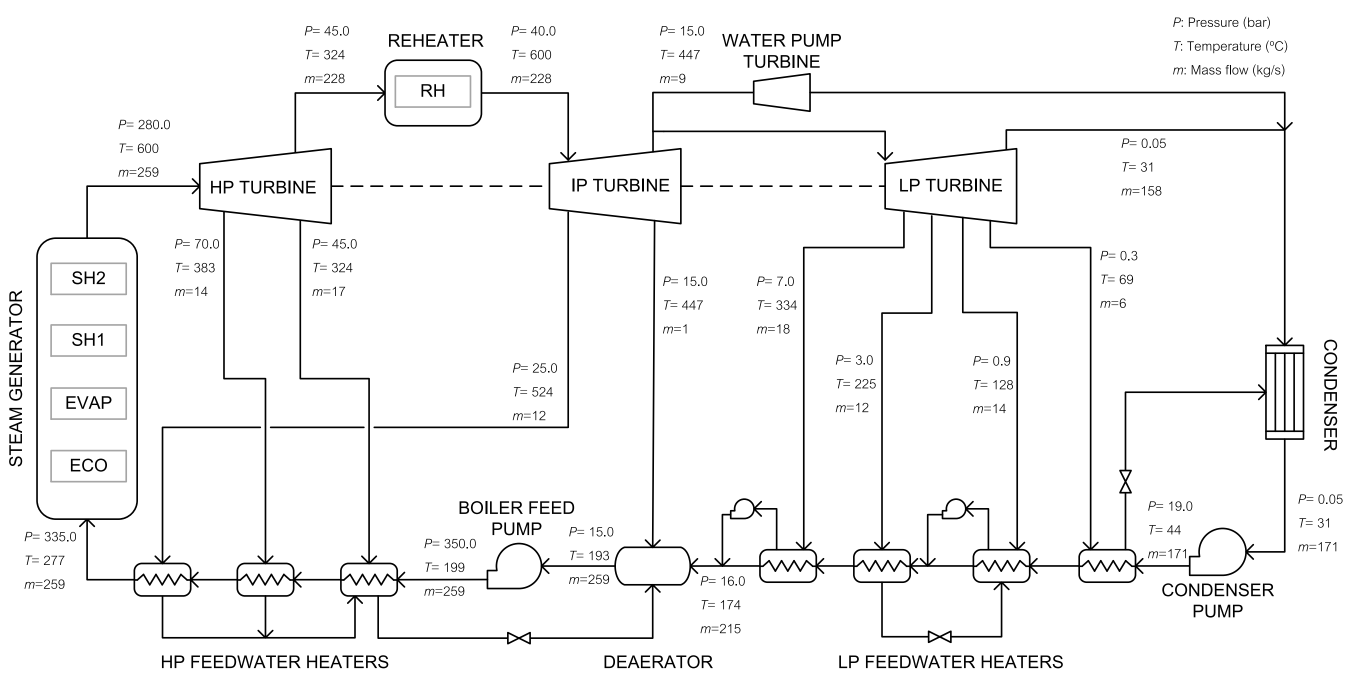


Figure 2. Reference power plant supercritical steam cycle. Pressure (P in bar) and temperature (T in °C) operation conditions. Mass flow (m in kg/s) reported correspond to a net electric power of 350 MW_e.

https://dx.doi.org/10.1021/acsomega.9b03552
ACS Omega 2020, 5, 4844−4852

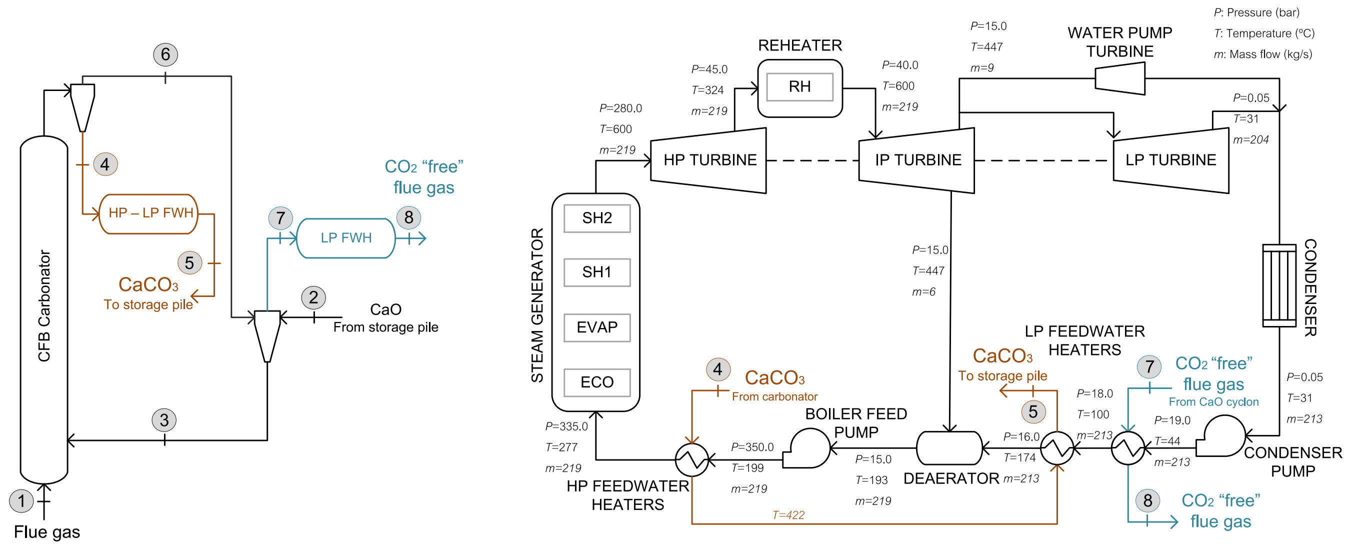


Figure 3. Carbonator block process scheme including the integration of the solids and gas streams (left) and the modified power plant supercritical steam cycle of Figure 2 where pressure (P in bar), temperature (T in °C), and mass flow (m in kg/s) operation conditions for the reference case are indicated (right).

looping pilot plants where the carbonator reactor is a CFB operated with active space times of around 20−80 s.[23,50,51]

The operation temperature of the adiabatic carbonator is directly linked to the conversion of the solids and the inlet temperature of the calcined solids entering the reactor. Several integration approaches can be put in practice to preheat the gas and solids streams entering the carbonator. These will ensure that, even for modest solid storage temperatures, standard temperatures of around 650 °C are achieved in the adiabatic carbonator during the steady-state operation mode thanks to the exothermic carbonation of CaO. In this way, the high-temperature heat available in the CO_2 "free" gas stream can be employed to heat up the flow of CaO stored at modest temperature before it enters into the carbonator reactor. Alternatively, the hot $CaCO_3$ leaving the carbonator reactor can be used to preheat the flue gas. These heat-exchange operations can be carried out by means of conventional gas−solid heat transfer methods or gas−solid cyclonic suspension preheaters, such as those available in cement plants.

For this specific case with a X_{ave} of 0.35, a solids inlet temperature of 410 °C is needed for the carbonator to operate at a temperature of 650 °C. This can be achieved by bringing the flue gas leaving the carbonator into contact with the solids coming from the CaO pile (as depicted in Figure 3), assuming that they have been stored at a temperature of 156 °C (please note that the CaO pile is feed from solids coming from the oxy-calciner reactor after recovering part of their heat for power production, as detailed in the following section). In comparison with the previously proposed scheme,[22] this preheating step allows the storage temperature in the CaO pile to be reduced by around 330 °C if the carbonator is operating at 650 °C. After this preheating step, the residual heat from the CO_2 flue gas and the heat available in the stream of carbonated solids leaving the carbonator can be integrated within the existing power plant steam cycle in the feedwater preheater sections, as schematically shown on the right-hand side of Figure 3. The heat available from the $CaCO_3$ stream can be used both in the high- and low-pressure feedwater heaters, thereby avoiding bleeds of steam from the high-, intermediate-, and part of the low-pressure turbines. The heat contained in the solids can be extracted in counter-current mode in moving bed heat exchangers (similar to that proposed by Nsakala et al.[52] for oxy-fired power plants). On the other hand, the waste heat available in the CO_2 "free" stream after the CaO preheating step can be used in the low-pressure feedwater preheater section by extracting heat in counter-current water−gas heat exchangers. In this way, all of the low pressure steam bleeds can be avoided. In both heat exchangers, the temperature of the water before entering the deaerator and the economizer has been kept constant as in the reference power plant and the outlet temperatures of the solids and gases have been calculated.

The use of heat from the gas and solids streams to heat up the water in the feedwater heaters allows the existing steam cycle to operate in two different ways, by increasing the effective power of the steam turbine or by reducing the power plant thermal input. On the one hand, the coal thermal input can be maintained at its nominal load of 777 MW_{th} and the extra carbonation heat can be used to boost the electrical power output from the power plant steam turbines. On the other hand, the coal thermal input in the back-up power plant can be reduced while producing the same electrical output of 350 MW_e as in the reference back-up power plant. One of the advantages of this second approach is that the amount of CO_2 produced during coal combustion decreases and, therefore, the size of the FlexiCaL elements and streams can be reduced. For these reasons, this second approach has been adopted in this study and the process of Figure 1 has been designed to produce the same net electrical output as in the reference power plant. Although there are some minor changes to the steam flow in the different turbine sections with respect to the reference case due to the absence of bleeds (<15%), the effect of these changes on the isentropic efficiencies of the steam turbine sections can be safely ignored and the same values of pressure and temperature as those shown in Figure 2 have been assumed.[53]

By following this second approach, the thermal power plant input can be reduced by 12% (i.e., down to 685 MW_{th}) with respect to the reference case. As is discussed in the following sections, the net efficiency of the whole FlexiCaL system will

https://dx.doi.org/10.1021/acsomega.9b03552
ACS Omega 2020, 5, 4844−4852

Table 2. Specifications of the Carbonator Block Streams (See Figure 3) for a Scenario with a Thermal Power Input to the Back-Up Power Plant of 685 MW_{th} and a X_{ave} = 0.35

					composition							
					solid (% wt)				gas (% v)			
nos	description	temperature (°C)	mass flow (kg/s)	heat available (MW_{th})[a]	CaO	$CaCO_3$	$CaSO_4$	Ash	CO_2	N_2	H_2O	O_2
1	flue gas from power plant	140	275.0	35.2					15.3	75.7	6.3	2.7
2	CaO from storage pile	156	267.7	32.6	94.6	0.0	4.2	1.2				
3	CaO entering carbonator	410		96.7								
4	$CaCO_3$ leaving carbonator	650	323.3	216.5	56.4	39.1	3.5	1.0				
5	$CaCO_3$ to storage pile	207		58.7								
6	CO_2 "free" gas leaving carbonator	650	219.3	166.1					1.8	87.8	7.3	3.1
7	CO_2 "free" gas to steam cycle	410		98.7								
8	exhaust CO_2 "free" gas	161		34.4								

[a]Reference temperature 20 °C.

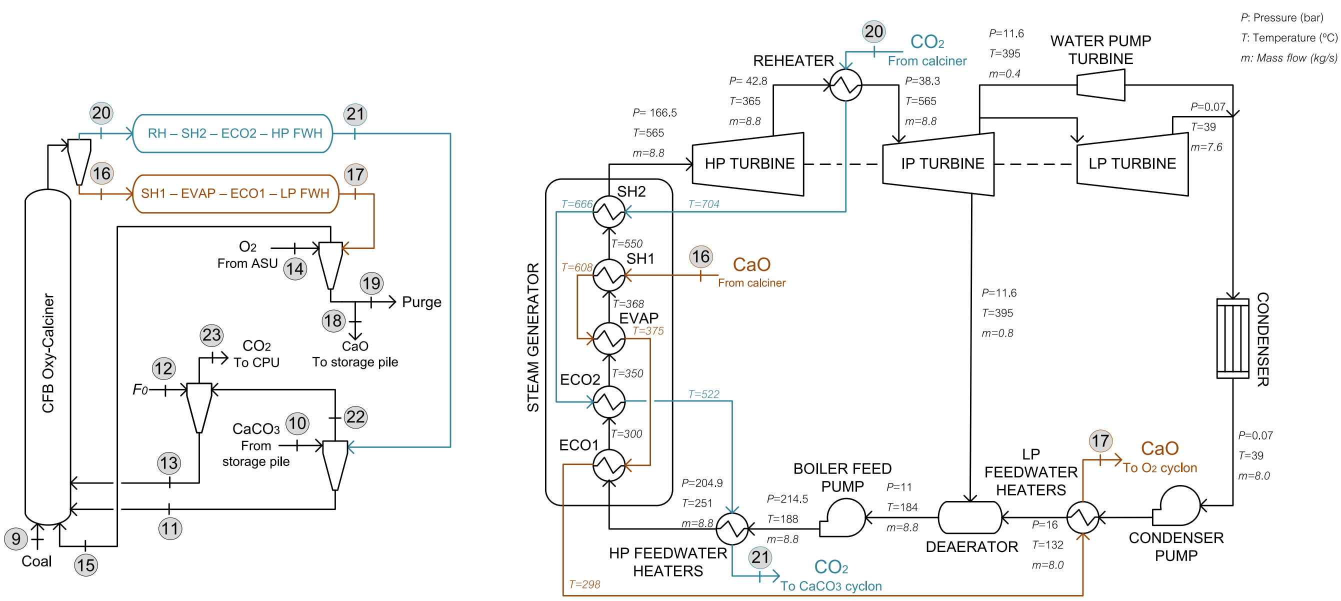


Figure 4. Oxy-calciner block integration of the solids and gas streams (left) and the sub-critical steam cycle (right). Pressure (P in bar) and temperature (T in °C) operation conditions for the steam cycle obtained from data available in the literature.[58,59] Mass flow (m in kg/s) reported for the reference case solved with an oxy-calciner gross electrical output of 12.5 MW_e.

be lower due to the penalty associated with the fuel requirements in the oxy-calciner block. This integration scheme makes it possible to transfer around 145 MW_{th} for water preheating in the steam cycle from the solids leaving the carbonator, which are cooled down to a temperature of 207 °C before being sent to the $CaCO_3$ pile. Meanwhile, the temperature of the CO_2 "free" gas stream is reduced to 161 °C before it is emitted, providing 61 MW_{th} for the low-pressure feedwater preheaters. As a result, a total amount of 206 MW_{th} from the carbonator block is used to produce power in the existing steam cycle. The elimination of steam bleeds from the turbine has a penalty effect on the net steam cycle efficiency (defined as the ratio between the net electrical power output and total thermal power input to the steam generator and feed water sections of the steam cycle) as this is reduced from 48% in the reference steam cycle of Figure 2 to 42% in the configuration shown in the right-hand side of Figure 3 where the steam bleeds from the turbines are avoided.[54] A summary of the main results of the balances solved for the carbonator block in the selected reference case is presented in Table 2 with the specifications of the process streams numbered in Figure 3.

3.3. Sorbent Regeneration and Thermal Integration of the Oxy-Calciner Block.

The equipment required for the regeneration of the sorbent includes a refractory adiabatic CFB combustor-calciner as well as an ASU that provides the required O_2 and a CO_2 compression and purification unit (CPU). The use of the solids piles allow to be operated in continuous mode. Thus, a continuous flow of carbonated solids is fed into the oxy-calciner from the $CaCO_3$ pile which acts as a buffer. As a result, a more reduced flow of solids goes from the $CaCO_3$ to the CaO pile through the oxy-calciner compared to the flow of calcined solids that is fed into the carbonator when the power plant is in operation. This also allows the size of the main components related with the calcination step to be reduced, as schematically shown in Figure 1; meanwhile, a modest flow of CO_2 is generated in steady state in the oxy-fired calciner. This should facilitate both the transport and storage of CO_2 because the range of

Table 3. Specifications of the Oxy-Calciner Block Streams (See Figure 4) for a Scenario with a Thermal Power Input to the Back-Up Power Plant of 685 MW_{th} and a X_{ave} = 0.35

					composition							
					solid (% wt)				gas (% v)			
no	description	temperature (°C)	mass flow (kg/s)	heat available (MW_{th})[a]	CaO	$CaCO_3$	$CaSO_4$	ash	CO_2	N_2	H_2O	O_2
9	coal to oxy-calciner	20	2.0	0.0	% wt (78.8 C, 4.7 H, 0.7 S, 5.8 O, 2.6 H_2O, 1.2 N, 6.2 ash)							
10	$CaCO_3$ from storage pile	207	32.3	5.9	56.4	39.1	3.5	1.0				
11	$CaCO_3$ entering oxy-calciner	270		7.9								
12	make-up flow (F_0)	20	5.2	0.0	0.0	100.0	0.0	0.0				
13	F_0 entering oxy-calciner	207		1.0								
14	O_2 from ASU	20	5.6	0.0					0.0	5.0	0.0	95.0
15	O_2 entering oxy-calciner	156		0.7								
16	CaO leaving oxy-calciner	910	29.8	26.3	94.6	0.0	4.2	1.2				
17	CaO after steam cycle	183		4.4								
18	CaO to storage pile	156	26.8	3.3								
19	Purge	156	3	0.4								
20	CO_2 leaving oxy-calciner	910	15.3	18.2					80.9	2.5	12.1	3.5
21	CO_2 after steam cycle	385		6.4								
22	CO_2 to F_0 pre-heater	270		4.1								
23	CO_2 to CPU	207		3.0								

[a]Reference temperature 20 °C.

geological CO_2 storage sites broadens thanks to the reduced amount of CO_2 to be stored per year.

To satisfy the electricity requirements of the ASU, CPU, and other auxiliary units associated with the oxy-calciner block, heat from the gas and solids streams leaving the oxy-calciner reactor can be recovered for power generation in a separate small steam cycle. After recovery, the remaining waste heat from these streams can be further employed to preheat the gas and solids entering the calciner in order to reduce the heat demand and fuel consumption, as below described. For the sake of simplicity, coal is assumed to be the fuel in the calciner. However, in future scenarios with a wider availability of renewable electricity, electrolytic hydrogen and oxygen could be available (as first pointed out by Steinbeck and Dettmann[55]) at a reasonable cost,[56] or other alternative biofuels could be employed to fire the small calciner required to regenerate the sorbent.

A temperature of 910 °C is considered to completely regenerate the $CaCO_3$ in the oxy-calciner reactor. Coal (78.8% C, 4.7% H, 0.7% S, 5.8% O, 2.6% H_2O, 1.2% N, and 6.2% ash, heating lower value of 32.5 MJ/kg) is burned using oxygen supplied from an ASU with a purity of 95% and in an excess of a 10%. In order to estimate the make-up flow of limestone (F_0), the equation proposed by Rodriguez et al.[57] has been used taking into account the effect of the CF on the average CO_2 flow fed into the carbonator (F_{CO_2}) as indicated in a previous work.[22] This yields a $F_0/(F_{CO_2}\mathrm{CF})$ ratio of 0.37 which translates into an annual limestone consumption of 0.16 Mton/year.

Most of the high-temperature heat available in the streams of gas and solids leaving the oxy-calciner reactor is used to produce power in a subcritical steam cycle, as shown in Figure 4. Pressure and temperature conditions in this cycle have been chosen in accordance with the data available in the literature.[58] To provide the required power for this subcritical steam cycle, heat is extracted from the CaO solids and CO_2-rich gas streams arriving from the oxy-calciner at a temperature of 910 °C in accordance with the scheme shown in the left-hand side of Figure 4. A minimum pinch temperature of 25 °C has been assumed in the different heat exchangers. In the proposed integration scheme, the heat contained in the CO_2-rich gas leaving the calciner is used in the reheating, superheating, economizer, and high-pressure feedwater preheater sections, which allows this stream to cool down to 385 °C. The waste heat from this gas stream is then recovered to preheat the stream of $CaCO_3$ solids and the make-up flow of limestone respectively before they enter the oxy-calciner. These heat exchanges steps allows the CO_2-rich flue gas stream temperature to be further reduced to 207 °C before it is sent to the CPU unit.

The heat contained in the calcined solids is also used in the superheating, evaporation, economizer, and low-pressure feedwater heater sections, as shown in Figure 4. This reduces the CaO stream temperature to 183 °C. In order to further cool down the solids and achieve the temperature needed in the CaO pile (i.e., 156 °C as discussed in Section 3.2), the waste heat can be employed to preheat the flow of O_2 fed into the oxy-calciner, as indicated in Figure 4. More detailed specifications of the process streams numbered in Figure 4 for the oxy-calciner block can be found in Table 3.

In accordance with previous assumptions and the integration scheme shown in Figures 3 and 4, a thermal input to the oxy-calciner as low as 66 MW_{th} is calculated. This represents a fraction of only 8% with respect to the total thermal capacity (including that of the back-up power plant). This compares favorably with conventional CaL systems that require a typical thermal capacity of around 45−50% for the oxy-fired calciner.[31] Another benefit of the system proposed is that a continuous flow of 0.31 kmol/s of CO_2 is produced in the calciner in contrast with the large flow of CO_2 captured from the power plant emitted during operation periods at a rate of 1.41 kmol/s. Consequently, the size of the CPU needed is reduced by almost 78%.

With the integration of Figure 4, a gross efficiency of 40% is calculated for the oxy-calciner block, resulting in a gross

https://dx.doi.org/10.1021/acsomega.9b03552
ACS Omega 2020, 5, 4844−4852

electrical power output ($P_{e\ gross,oxy\text{-}calciner}$) of 12.5 MW_e. On the basis of typical assumptions for power consumption in the main elements of the oxy-calciner block (i.e., 5% of the gross power output in the auxiliaries[60] and 200 kWh_e/t_{O_2} and 120 kWh_e/t_{CO_2} in the ASU and CPU units, respectively[61]), an internal consumption of around 11 MW_e is estimated for the oxy-calciner block. Thus, it can be assumed that no net power is produced by the steam cycle associated with the calciner. The power delivered to the grid comes only from the steam cycle associated with the back-up power plant and carbonator blocks.

3.4. Global Process Performance. Accordingly to the discussion of the previous sections, the net efficiency of the FlexiCaL system ($\eta_{FlexiCaL}$) as depicted in Figure 1, exporting power only during a fraction of the time CF and considering that the net power output is zero from the oxy-calciner thermal input, can be calculated using the following equation

$$\eta_{FlexiCaL} = ((P_{e,net}CF)/(P_{th,power\ plant}CF + P_{th,oxy\text{-}calciner} - P_{th,F_0}))\cdot 100 \quad (1)$$

where $P_{e,net}$ is the net electrical power produced in the system and $P_{th,power\ plant}$ and $P_{th,oxy\text{-}calciner}$ are the thermal inputs to the power plant and the oxy-fired calciner, respectively, and reported in the previous sections. The thermal input associated with the calcination of the fresh limestone (P_{th,F_0}) can be discounted considering the benefits from the potential use of the CaO-rich purge (around 0.1 Mton/year) in a cement plant or another large-scale CaO consumer. From eq 1, a $\eta_{FlexiCaL}$ of 28% is calculated; meanwhile, the net power efficiency of the reference power plant without CO_2 capture was of 45%. Despite this modest value it should be emphasized that the energy penalty related to the regeneration of the sorbent is applied during the whole operating period, while the back-up power plant is able to deliver a net power output of 350 MW_e to the grid when it is required to enter into operation and capturing the CO_2 in the flue gas with a 90% efficiency.

Regarding the capacity of the CaO and $CaCO_3$ piles depicted in Figure 1, around 20 800 and 25 100 m^3, respectively, (assuming a bulk density of 1000 kg/m^3) are needed per operation day of the back-up power plant. As mentioned above, for the integration scheme proposed, the CaO and $CaCO_3$ are stored at temperatures of around 150–200 °C. This facilitates the solid handling and storage operations by making it possible to use equipment normally employed in other processes (e.g., in the cement industry).[22]

Finally, the main process parameters of the reference case solved in the previous sections have been summarized in Table 4. The reference case here studied shows that the FlexiCaL process configuration represents a promising CO_2 capture system for retrofitting and extending the lifetime of amortized back-up fossil fuel power plants forced to operate under extremely low-capacity factors.

4. CONCLUSIONS

Calcium looping system relying on large reservoirs of low-temperature $CaCO_3$ and CaO can be used to capture the CO_2 emitted from existing back-up coal power plant forced to operate under extremely low CFs. One of the main features of the FlexiCaL process is the use of existing equipment in the power plant to minimize the need of additional equipment associated with the CO_2 capture and to avoid waste of capital.

Table 4. Summary of the Global Performance of the FlexiCaL Reference Case Studied in This Work

description	unit	value
net electrical power output, $P_{e,net}$	MW_e	350
power plant thermal input, $P_{th,power\ plant}$	MW_{th}	685
power recovered from carbonator block to the power plant steam cycle, $P_{th,carbonator}$	MW_{th}	206
oxy-calciner thermal input, $P_{th,oxy\text{-}calciner}$	MW_{th}	66
oxy-calciner block gross electrical power output, $P_{e\ gross,oxy\text{-}calciner}$	MW_e	12.5
net efficiency of the FlexiCaL system (eq 1), $\eta_{FlexiCaL}$	%	28
storage silos capacity, $V_{storage}$	m^3/day	20 800–25 100

The thermal integration exercise carried out reveals that it is possible to maintain the net power output of the back-up plant with capture, by sacrificing the efficiency of the system when regenerating the $CaCO_3$ to CaO. This is because the proposed system includes an adiabatic carbonator reactor that can follow the power plant operation periods, whereas the small-scale oxy-calciner block produces power for the autoconsumption in the air separation and compression units (i.e., zero net power exports). A reference case solved for a CF of 0.1 indicates that 12% of the energy during back-up power operations comes from the heat recovered from the carbonator block when using the feedwater preheater sections of the existing power plant steam cycle. For a reference output of 350 MW_e, and assuming a reasonable solids storage activity (X_{ave} of 0.35), a thermal input of just 66 MW_{th} (which represents only 8% of the total thermal capacity of the system) is required in the oxy-calciner block to achieve the complete regeneration of the carbonated solids, storing the solids at moderate temperatures of around 150–200 °C. A large volume of solid reservoirs is needed (around 20 000–25 000 m^3 of bulk solids per day operating at full load), but the very low specific cost of CaO and $CaCO_3$ materials could make this process attractive in future scenarios where capture of CO_2 from back-up power plants may be needed.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b03552.

Composite curves of the carbonator and oxy-calciner gas and solids streams integration with their corresponding steam cycles (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Yolanda A. Criado – *CSIC-INCAR 33011 Oviedo, Spain;* orcid.org/0000-0003-2962-7061; Phone: +34 985119090; Email: yolanda.ac@incar.csic.es; Fax: +34 985297662

Authors

Borja Arias – *CSIC-INCAR 33011 Oviedo, Spain*

J. Carlos Abanades – *CSIC-INCAR 33011 Oviedo, Spain*

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.9b03552

Notes

The authors declare no competing financial interest.

https://dx.doi.org/10.1021/acsomega.9b03552
ACS Omega 2020, 5, 4844–4852

ACKNOWLEDGMENTS

The authors acknowledge the financial support provided by the European Union under the Research Fund for Coal and Steel (RFCS) Program (FlexiCaL project, no. 709629), the Spanish Ministry of Science, Innovation and Universities (RTI2018-097224-B-I00) and the FEDER Funds of the Principality of Asturias (IDI/2018/000138).

NOMENCLATURE

CF	capacity factor
E_{calc}	calcination efficiency
E_{carb}	CO_2 capture efficiency
F_0	make-up flow, mol/s
F_{CO_2}	average CO_2 flow fed into the carbonator, mol/s
m	mass flow, kg/s
P	pressure of steam cycle streams, bar
$P_{e,net}$	net electrical power output, MW_e
$P_{e\ gross,oxy\text{-}calciner}$	oxy-calciner block gross electrical power output, MW_e
$P_{th,carbonator}$	power recovered from carbonator block to the power plant, MW_{th}
P_{th,F_0}	thermal input associated with the calcination of F_0, MW_{th}
$P_{th,oxy\text{-}calciner}$	oxy-calciner thermal input, MW_{th}
$P_{th,power\ plant\ ref}$	power plant thermal capacity, MW_{th}
$P_{th,power\ plant}$	power plant thermal input, MW_{th}
T	temperature, °C
T_{calc}	oxy-calcination temperature, °C
T_{carb}	carbonator temperature, °C
$V_{storage}$	storage silos capacity, m^3/day
X_{ave}	average CO_2 carrying capacity
$\eta_{FlexiCaL}$	net efficiency of the FlexiCaL system according to eq 1, %
$\eta_{power\ plant}$	net efficiency of the reference power plant without CO_2 capture, %

REFERENCES

(1) *IEA Energy Technology Perspectives 2017*; International Energy Agency: Paris, France, 2017.

(2) REN21 Renewables Global Futures Report. *Great Debates towards 100% Renewable Energy*; Renewable Energy Police Network for the 21st Century: Paris, France, 2017.

(3) IEA. Harnessing variable renewables. *A Guide to the Balancing Challenge*; International Energy Agency: Paris, France, 2011.

(4) Kumar, N.; Besuner, P.; Lefton, S.; Agan, D. *Power Plant Cycling Costs*; National Renewable Laboratory, 2012.

(5) Keatley, P.; Shibli, A.; Hewitt, N. J. Estimating power plant start costs in cyclic operation. *Appl. Energy* **2013**, *111*, 550.

(6) Montañés, R. M.; KorpÅs, M.; Nord, L. O.; Jaehnert, S. Identifying operational requirements for flexible CCS power plant in future energy systems. *Energy Procedia* **2016**, *86*, 22.

(7) *UNFCCC Report of the Conference of the Parties on its 21st Session: Decisions Adopted by the Conference of the Parties*; United Nations Framework Convention on Climate Change, 2016.

(8) Davison, J. Flexible CCS plants—A key to near-zero emission electricity systems. *Energy Procedia* **2011**, *4*, 2548.

(9) Domenichini, R.; Mancuso, L.; Ferrari, N.; Davison, J. John Operating flexibility of power plants with carbon capture and storage (CCS). *Energy Procedia* **2013**, *37*, 2727.

(10) Chalmers, H.; Gibbins, J.; Leach, M. Matt Valuing power plant flexibility with CCS: the case of post-combustion capture retrofits. *Mitig. Adapt. Strategies Glob. Change* **2012**, *17*, 621.

(11) IEAGHG. *Operating Flexibility of Power Plants with CCS*; International Energy Agency Greenhouse Gas R&D Programme, 2012.

(12) Mac Dowell, N.; Staffell, I. The role of flexible CCS in the UK's future energy system. *Int. J. Greenhouse Gas Control* **2016**, *48*, 327.

(13) ZEP Future CCS technologies. *European Technology Platform for Zero Emissions Fossil Fuel Power Plants*, 2017.

(14) Abdilahi, A. M.; Mustafa, M. W.; Abujarad, S. Y.; Mustapha, M. Harnessing flexibility potential of flexible carbon capture power plants for future low carbon power systems: Review. *Renewable Sustainable Energy Rev.* **2018**, *81*, 3101.

(15) Sanchez Fernandez, E.; Sanchez del Rio, M.; Chalmers, H.; Khakharia, P.; Goetheer, E. L. V.; Gibbins, J.; Lucquiaud, M. Operational flexibility options in power plants with integrated post-combustion capture. *Int. J. Greenhouse Gas Control* **2016**, *48*, 275.

(16) Craig, M. T.; Zhai, H.; Jaramillo, P.; Klima, K. Trade-offs in cost and emission reductions between flexible and normal carbon capture and sequestration under carbon dioxide emission constraints. *Int. J. Greenhouse Gas Control* **2017**, *66*, 25.

(17) Perrin, N.; Dubettier, R.; Lockwood, F.; Tranier, J.-P.; Bourhy-Weber, C.; Terrien, P. Oxycombustion for coal power plants: Advantages, solutions and projects. *Appl. Therm. Eng.* **2015**, *74*, 75.

(18) Hanak, D. P.; Powell, D.; Manovic, V. Techno-economic analysis of oxy-combustion coal-fired power plant with cryogenic oxygen storage. *Appl. Energy* **2017**, *191*, 193.

(19) Zhou, L.; Duan, L.; Anthony, E. J. A calcium looping process for simultaneous CO_2 capture and peak shaving in a coal-fired power plant. *Appl. Energy* **2019**, *235*, 480.

(20) ETI *Hydrogen: The Role of Hydrogen Storage in a Clean Responsive Power System*; Energy Technologies Institute: United Kingdom, 2015.

(21) Davison, J.; Arienti, S.; Cotone, P.; Mancuso, L. Co-production of hydrogen and electricity with CO_2 capture. *Energy Procedia* **2009**, *1*, 4063.

(22) Criado, Y. A.; Arias, B.; Abanades, J. C. Calcium looping CO_2 capture system for back-up power plants. *Energy Environ. Sci.* **2017**, *10*, 1994.

(23) Arias, B.; Diego, M. E.; Méndez, A.; Alonso, M.; Abanades, J. C. Calcium looping performance under extreme oxy-fuel combustion conditions in the calciner. *Fuel* **2018**, *222*, 711.

(24) Dieter, H.; Bidwe, A. R.; Varela-Duelli, G.; Charitos, A.; Hawthorne, C.; Scheffknecht, G. Development of the calcium looping CO_2 capture technology from lab to pilot scale at IFK, University of Stuttgart. *Fuel* **2014**, *127*, 23.

(25) Chang, M.-H.; Chen, W.-C.; Huang, C.-M.; Liu, W.-H.; Chou, Y.-C.; Chang, W.-C.; Chen, W.; Cheng, J.-Y.; Huang, K.-E.; Hsu, H.-W. Design and experimental testing of a 1.9 MW_{th} calcium looping pilot plant. *Energy Procedia* **2014**, *63*, 2100.

(26) Arias, B.; Diego, M. E.; Abanades, J. C.; Lorenzo, M.; Diaz, L.; Martínez, D.; Alvarez, J.; Sánchez-Biezma, A. Demonstration of steady state CO_2 capture in a 1.7 MW_{th} calcium looping pilot. *Int. J. Greenhouse Gas Control* **2013**, *18*, 237.

(27) Alonso, M.; Diego, M. E.; Pérez, C.; Chamberlain, J. R.; Abanades, J. C. Biomass combustion with in situ CO_2 capture by CaO in a 300 kW_{th} circulating fluidized bed facility. *Int. J. Greenhouse Gas Control* **2014**, *29*, 142.

(28) Kremer, J.; Galloy, A.; Ströhle, J.; Epple, B. Continuous CO_2 capture in a 1-MW_{th} carbonate looping pilot plant. *Chem. Eng. Technol.* **2013**, *36*, 1518.

(29) Abanades, J. C.; Arias, B.; Lyngfelt, A.; Mattisson, T.; Wiley, D. E.; Li, H.; Ho, M. T.; Mangano, E.; Brandani, S. Emerging CO_2 capture systems. *Int. J. Greenhouse Gas Control* **2015**, *40*, 126.

(30) Hanak, D. P.; Anthony, E. J.; Manovic, V. A review of developments in pilot-plant testing and modelling of calcium looping process for CO_2 capture from power generation systems. *Energy Environ. Sci.* **2015**, *8*, 2199.

(31) Martínez, I.; Grasa, G.; Parkkinen, J.; Tynjälä, T.; Hyppänen, T.; Murillo, R.; Romano, M. C. Review and research needs of Ca-

Looping systems modelling for post-combustion CO_2 capture applications. *Int. J. Greenhouse Gas Control* **2016**, *50*, 271.
(32) Arias, I. M. B.; Arias, B.; Grasa, G. S.; Abanades, J. C. CO_2 capture in existing power plants using second generation Ca-Looping systems firing biomass in the calciner. *J. Clean. Prod.* **2018**, *187*, 638.
(33) Mantripragada, H. C.; Rubin, E. S. Calcium Looping cycle for CO_2 capture: Performance, cost and feasibility analysis. *Energy Procedia* **2014**, *63*, 2199.
(34) Perejón, A.; Romeo, L. M.; Lara, Y.; Lisbona, P.; Martínez, A.; Valverde, J. M. The Calcium-Looping technology for CO_2 capture: On the important roles of energy integration and sorbent behavior. *Appl. Energy* **2016**, *162*, 787.
(35) Hawthorne, C.; Trossmann, M.; Galindo Cifre, P.; Schuster, A.; Scheffknecht, G. Simulation of the carbonate looping power cycle. *Energy Procedia* **2009**, *1*, 1387.
(36) Yang, Y.; Zhai, R.; Duan, L.; Kavosh, M.; Patchigolla, K.; Oakey, J. Integration and evaluation of a power plant with a CaO-based CO_2 capture system. *Int. J. Greenhouse Gas Control* **2010**, *4*, 603.
(37) Ströhle, J.; Lasheras, A.; Galloy, A.; Epple, B. Simulation of the carbonate looping process for post-combustion CO_2 capture from a coal-fired power plant. *Chem. Eng. Technol.* **2009**, *32*, 435.
(38) Hu, Y.; Ahn, H. Process integration of a Calcium-looping process with a natural gas combined cycle power plant for CO_2 capture and its improvement by exhaust gas recirculation. *Appl. Energy* **2017**, *187*, 480.
(39) Rubin, E. S.; Short, C.; Booras, G.; Davison, J.; Ekstrom, C.; Matuszewski, M.; McCoy, S. A proposed methodology for CO_2 capture and storage cost estimates. *Int. J. Greenhouse Gas Control* **2013**, *17*, 488.
(40) Ozcan, D. C.; Alonso, M.; Ahn, H.; Abanades, J. C.; Brandani, S. Process and cost analysis of a biomass power plant with in situ Calcium Looping CO_2 capture process. *Ind. Eng. Chem. Res.* **2014**, *53*, 10721.
(41) Guandalini, G.; Romano, M. C.; Ho, M.; Wiley, D.; Rubin, E. S.; Abanades, J. C. A sequential approach for the economic evaluation of new CO_2 capture technologies for power plants. *Int. J. Greenhouse Gas Control* **2019**, *84*, 219.
(42) Ylätalo, J.; Ritvanen, J.; Arias, B.; Tynjälä, T.; Hyppänen, T. 1-Dimensional modelling and simulation of the calcium looping process. *Int. J. Greenhouse Gas Control* **2012**, *9*, 130.
(43) Ylätalo, J.; Ritvanen, J.; Tynjälä, T.; Hyppänen, T. Model based scale-up study of the calcium looping process. *Fuel* **2014**, *115*, 329.
(44) Cormos, A.-M.; Simon, A. Assessment of CO_2 capture by calcium looping (CaL) process in a flexible power plant operation scenario. *Appl. Therm. Eng.* **2015**, *80*, 319.
(45) Astolfi, M.; De Lena, E.; Romano, M. C. Improved flexibility and economics of Calcium Looping power plants by thermochemical energy storage. *Int. J. Greenhouse Gas Control* **2019**, *83*, 140.
(46) Hanak, D. P.; Biliyok, C.; Manovic, V. Calcium looping with inherent energy storage for decarbonisation of coal-fired power plant. *Energy Environ. Sci.* **2016**, *9*, 971.
(47) Ortiz, C.; Romano, M. C.; Valverde, J. M.; Binotti, M.; Chacartegui, R. Process integration of Calcium-Looping thermochemical energy storage system in concentrating solar power plants. *Energy* **2018**, *155*, 535.
(48) Shimizu, T.; Hirama, T.; Hosoda, H.; Kitano, K.; Inagaki, M.; Tejima, K. A twin fluid-bed reactor for removal of CO_2 from combustion processes. *Chem. Eng. Res. Des.* **1999**, *77*, 62.
(49) DOE/NETL. *Cost and Performance Baseline for Fossil Energy Plants Volume 1a: Bituminous Coal (PC) and Natural Gas to Electricity*. Revision 3.; DOE/NETL-2015/1723; US Department of Energy, National Energy Technology Laboratory, 2015.
(50) Charitos, A.; Rodríguez, N.; Hawthorne, C.; Alonso, M.; Zieba, M.; Arias, B.; Kopanakis, G.; Scheffknecht, G.; Abanades, J. C. Experimental validation of the Calcium Looping CO_2 capture process with two circulating fluidized bed carbonator reactors. *Ind. Eng. Chem. Res.* **2011**, *50*, 9685.
(51) Hilz, J.; Helbig, M.; Haaf, M.; Daikeler, A.; Ströhle, J.; Epple, B. Long-term pilot testing of the carbonate looping process in $1MW_{th}$ scale. *Fuel* **2017**, *210*, 892.
(52) Nsakala, N.; Liljedahl, G. N.; Turek, D. *Greenhouse Gas Emissions Control by Oxygen Firing in Circulating Fluidized Bed Boilers-Phase II. Final Technical Progress Report*; Alstom Power Inc., 2004.
(53) IEA. *Power Generation from Coal: Measuring and Reporting Efficiency Performance and CO_2 Emissions*; International Energy Agency - Coal Industry Advisory Board (CIAB): France, 2010.
(54) Kitto, J. B.; Stultz, S. C. *Steam, its Generation and Use*, 41st ed.; The Babcok &Wilcox Company: Barberton, OH, USA., 2005.
(55) Steinbeck, J.; Dettmann, K. Energy loss of fast H^{2+} molecules in solids. I. *J. Phys. C: Solid State Phys.* **1978**, *11*, 2907.
(56) Davis, S. J.; Lewis, N. S.; Shaner, M.; Aggarwal, S.; Arent, D.; Azevedo, I. L.; Benson, S. M.; Bradley, T.; Brouwer, J.; Chiang, Y.-M.; Clack, C. T. M.; Cohen, A.; Doig, S.; Edmonds, J.; Fennell, P.; Field, C. B.; Hannegan, B.; Hodge, B.-M.; Hoffert, M. I.; Ingersoll, E.; Jaramillo, P.; Lackner, K. S.; Mach, K. J.; Mastrandrea, M.; Ogden, J.; Peterson, P. F.; Sanchez, D. L.; Sperling, D.; Stagner, J.; Trancik, J. E.; Yang, C.-J.; Caldeira, K. Net-zero emissions energy systems. *Science* **2018**, *360*, No. eaas9793.
(57) Rodríguez, N.; Alonso, M.; Abanades, J. C. Average activity of CaO particles in a calcium looping system. *Chem. Eng. J.* **2010**, *156*, 388.
(58) DOE/NETL. *Cost and Performance Baseline for Fossil Energy Plants, Volume 1: Bituminous Coal and Natural Gas to Electricity*. Final Report: 2007/1281; US Department of Energy, National Energy Technology Laboratory, 2007.
(59) Nsakala, N.; Liljedahl, G. N.; Marion, J.; Levasseur, A. A.; Turek, D.; Chamberland, R.; MacWhinnie, R. Oxygen-fired circulating fluidized bed boilers for greenhouse gas emissions control and other applications. *3rd Conference on Carbon Capture Sequestration, Alexandria, Virginia*, 2004.
(60) Romeo, L. M.; Abanades, J. C.; Escosa, J. M.; Paño, J.; Giménez, A.; Sánchez-Biezma, A.; Ballesteros, J. C. Oxyfuel carbonation/calcination cycle for low cost CO_2 capture in existing power plants. *Energy Convers. Manage.* **2008**, *49*, 2809.
(61) Darde, A.; Prabhakar, R.; Tranier, J.-P.; Perrin, N. Nicolas Air separation and flue gas compression and purification units for oxy-coal combustion systems. *Energy Procedia* **2009**, *1*, 527.

https://dx.doi.org/10.1021/acsomega.9b03552
ACS Omega 2020, 5, 4844−4852