Integration of a Ca Looping System for CO_2 Capture in Existing Power Plants

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This work analyses a Ca looping system that uses CaO as regenerable sorbent to capture CO_2 from the flue gases generated in power plants. The CO_2 is captured by CaO in a CFB carbonator while coal oxycombustion provides the energy required to regenerate the sorbent. Part of the energy introduced into the calciner can be transferred to a new supercritical steam cycle to generate additional power. Several case studies have been integrated with this steam cycle. Efficiency penalties, mainly associated with the energy consumption of the ASU, CO_2 compressor and auxiliaries, can be as low as 7.5% p. of net efficiency when working with low-$CaCO_3$ make-up flows and integrating the Ca looping with a cement plant that makes use of the spent sorbent. The penalties increase to 8.3% p. when this possibility is not available. Operation conditions aiming at minimum calciner size result in slightly higher-efficiency penalties. © 2010 American Institute of Chemical Engineers AIChE J, 57: 2599–2607, 2011
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Introduction

Fossil fuels account for 85% of total anthropogenic CO_2 emissions. A large proportion ($\sim$25%) of these emissions comes from coal combustion for thermal and electrical energy production. Coal is expected to be a prominent fuel for electricity production in the medium term[1] because it is cheaper, easier to transport, and more abundant than oil and natural gas. In addition, it is a widespread resource distributed all over the world.

CO_2 capture and storage (CCS) has been identified as a potential technology to continue using fossil fuels in a CO_2 emission constrained world.[2] Among the different CCS technologies, postcombustion ones are the only options for the retrofitting of existing power plants. Here, we refer to those recently built or under construction, as those that are too old and with low efficiency are not suitable for CCS.[2] In principle, the operation of a power plant with a postcombustion capture system is not affected by the installation and operation of CCS system. Amine-based absorption processes have been proven commercially for postcombustion CO_2 capture systems,[2,3] although they still need some optimization and scaling up. However, the energy needed for the monoethanolamine regeneration step results in large inherent efficiency penalties that contribute to make the process economically unattractive at present. For this reason, emerging postcombustion technologies using alternative solvents or solid sorbents[2] are under development.

This work focuses on the Ca looping system for CO_2 capture that was originally proposed by Shimizu et al.,[4] using lime as CO_2-sorbent. The system involves the separation of CO_2 using the reversible carbonation reaction of CaO and
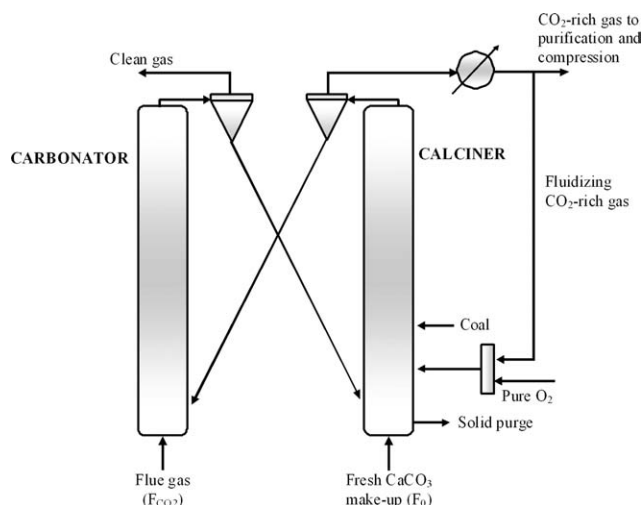
Figure 1. Conceptual scheme of the Ca looping system for CO₂ capture.

the calcination of $CaCO_3$ to regenerate the sorbent. As can be observed in the process scheme depicted in Figure 1, this process takes place in two interconnected circulating fluidized beds (calciner and carbonator) operating under atmospheric pressure. Flue gases leaving the boiler of an existing power plant are fed into the carbonation unit where the CO_2 reacts with the CaO coming from the calciner to obtain $CaCO_3$. Solids from carbonator are sent back to the calcination unit where $CaCO_3$ is again decomposed to form CaO, which is recirculated to the carbonator, and CO_2 as a concentrated gas stream suitable for compression and storage. Since a nearly pure CO_2 stream is needed from the calciner, operation at high-temperature ($\sim$950°C) is required for calcination, and oxyfuel combustion of coal can be used to supply the calcination energy. Much research has been reported with respect to the sorbent performance[5–13] and the appropriate operating conditions according to the energy required in this capture system.[14] It has been demonstrated that a Ca looping system involves a lower-efficiency penalty in the existing plant than other CO_2 capture technologies.[4,15–17] The efficiency of the Ca looping system relies on the possibility of recovering the energy introduced in the regeneration step that is released at high-temperatures and can be used to produce additional power in a new steam cycle. Highly integrated systems between an existing power plant and the capture system have been described to minimize the efficiency penalty, through an exergy analysis[17] or, by reducing the coal consumption of the original power plant resulting from the integration of the energy from the Ca looping in the existing steam cycle.[18] Conversely to the integration described in this work, the systems described in the literature propose the modification of operating conditions in the turbines and in the water heaters of the original power plant.

Few articles deal with the integration of a Ca looping system into an existing power plant not involving operational modifications that affect its functioning. In an initial work, Romeo et al. (2008)[19] proposed the application of this capture system to a supercritical coal-fired power plant including a new supercritical steam cycle, to take advantage of the

heat released in the capture system and to produce additional power output. It was proposed that the capture system variables should be fixed to achieve 85% CO_2 capture efficiency with a CaO/CO_2 mol fraction of 5. These assumptions have proven critical for defining the heat requirements in the calciner and the overall performance of the system,[14,16–18] and they are heavily interlinked with external variables such as the make-up flow and the solid circulation rate between reactors. Recently, mass and energy balances of a Ca looping system integrated with a supercritical steam cycle have been solved by studying the economical impact of solids purging on the tonne CO_2 avoided cost.[20] It was concluded that the amount of purged material had great effect on the cost of CO_2 avoided, and, although it was always competitive with respect to other technologies, it was minimized by working with low-purge streams.

The purpose of the present work is to determine the operating conditions in a Ca looping cycle that minimize the energy penalty when this CO_2 capture system is implemented in an existing subcritical coal-fired power plant with 36% net efficiency. Mass and energy balances of the Ca looping system are solved and better linked, with more realistic models for the carbonator reactor to select the optimum conditions for thermal integration with a new supercritical steam cycle. An Aspen Hysys® model of the coal-fired subcritical power plant plus the capture system has been developed, and the efficiency penalty owing to the capture and CO_2 compression system has been estimated as a function of operating conditions.

Process Description

Capture system

The results presented in this article are steady-state simulations referring to case studies where a coal-fired boiler of an existing power plant is simulated together with a CO_2 capture system. A subcritical power plant producing an output of 350 MW with a 36% net efficiency has been chosen as a reference. This power plant burns $\sim$200 tonnes/h of coal with an 86.5% boiler thermal efficiency and an air excess of 15%. After energy recovery, the exhaust gas is sent to an existing desulfurization unit and finally to the CO_2 capture system under typical stack conditions. Conversely to other capture technologies, an advantage of the Ca looping system is that the affinity of CaO toward sulfur compounds would make a flue-gas desulfurization unit unnecessary before the CO_2 capture system. However, we assume in this work that the existing power plant is equipped with desulfurization equipment that removes 90% of the SO_2 in the flue gas. Moreover, the solids purged from the process, mainly consisting of deactivated CaO and $CaSO_4$, could be used in the cement industry[21] as a raw material in clinker manufacture.

The characteristics of the flue gas that enters the carbonation unit of the CO_2 capture system propelled by a forced draft fan are shown in Table 1. The circulating fluidized bed reactors corresponding to the carbonation and calcination units are implemented in Aspen Hysys® as explained below.

Carbonator. The CO_2 coming from the existing power plant is captured in this reactor by the CaO generated in the calciner. It can be designed as a circulating fluidized bed

Table 1. Description of the Flue Gas Generated in the Existing Power Plant and the Coal Burnt in the Calciner

Flue Gas from Power Plant		Coal in the Calciner	
Mass Flow (kg/s)	446	Composition (%, wet basis)	
Temperature (°C)	180	C	66.30
Pressure (kPa)	116	H	3.60
Composition (% vol)		N	1.60
CO_2	14.50	O	7.00
H_2O	9.40	S	0.60
SO_2	0.04	Ash	14.20
O_2	2.50	Moisture	6.70
N_2	73.50	LHV (MJ/kg)	25.27

reactor where part of the solids generated in the calciner at 950°C are fluidized by the flue-gas stream produced in the existing power plant. This reactor operates at atmospheric pressure and 650°C, because the CO_2 partial pressure in equilibrium with the CaO is sufficiently low (1.22 kPa) to achieve high-carbonation efficiency. A basic carbonator reactor model that considers the instantaneous and perfect mixing of the solids, the plug flow for the gas-phase in the reactor and a gas–solid reaction model for the CaO particles[22] has been implemented. Furthermore, this reactor model has been improved by including a kinetic mechanistic model based on Bathia and Perlmutter's kinetic model.[23] This model considers that the carbonation reaction takes place in two stages: an initial fast reaction stage controlled by chemical reaction and a second slower stage controlled by both chemical reaction and CO_2 diffusion the product layer. This model has been recently adapted to multiple reaction cycles.[12] To carry out the mass balance in the carbonator reactor, the residence time distribution of particles in the system and the number of times that solids circulate between reactors has been considered. The model also considers the fact that, due to residence time and kinetics, the CaO particles may not achieve its maximum conversion on every cycle. According to the results from a recent article that refines the mass balances in the system from Figure 1, the decay of CaO carbonation capacity with the number of cycles is reduced when the sorbent is partially converted on every cycle.[24]

CO_2 capture efficiencies of 70, 80, and 90% were established as an objective for this unit in the different simulations. The carbonation reactor model has two independent variables that need to be changed to provide a given CO_2 capture efficiency. The first independent variable is the CaO inventory in the reactor, which affects the residence time distribution of the particles in the system and, subsequently, the carbonation conversion reached. The second independent variable is the fresh $CaCO_3$ make-up flow introduced in the calciner to maintain the CaO particle activity in the system. This variable determines the solid circulation rate between reactors that is needed to achieve the desired carbonation efficiency.

Calciner. The aim of this reactor is to calcine the $CaCO_3$ formed in the carbonation unit and the $CaCO_3$ coming from the fresh make-up flow. This reactor could be designed as a circulating fluidized bed reactor operating at atmospheric pressure and 950°C to ensure total $CaCO_3$ calcination even under a rich CO_2 atmosphere (equilibrium partial pressure of

CO_2 on CaO at 950°C corresponds to 196 kPa). The calciner is implemented in the simulation model as a conversion reactor operating adiabatically, where total $CaCO_3$ calcination is achieved. To supply the energy needed to regenerate the sorbent and to heat the solids coming from the carbonator at 650°C, a typical South African coal is burnt in the calciner. The coal composition and its lower-heating value are shown in Table 1. Despite the low-sulfur content of the coal burnt in the calciner and the desulfurization unit operating at the existing power plant, a minimum flow of $CaCO_3$ has to be supplied to the system to react with the SO_2 from coal combustion in the calciner and the SO_2 from the flue gas in the carbonator. To calculate the molar flow of this extra $CaCO_3$, a molar Ca/S ratio of 3 has been considered. This stream is fed to the calciner together with the fresh $CaCO_3$ make-up flow considered above. Furthermore, it has been assumed that 40% of the coal ash is separated as fly ash in the calciner secondary cyclones containing 5% unburned material. The gas stream that leaves the calciner has a high-CO_2 concentration, as the calciner operates as an oxyfuel combustor considering a 5% of combustion excess O_2 with respect to the stoichiometric in the combustion reaction. Part of the rich CO_2 stream obtained as product is split and recirculated, maintaining 25% O_2 in the gas-inlet stream. The CO_2-rich gas stream that leaves the calciner is cooled down to ∼150°C, which allows an energy recovery stage to be implemented. This stream is subsequently split into the fluidizing CO_2 and the CO_2 that goes to the purification and compression stage (see Figure 1). To prevent ash and deactivated sorbent accumulation in the system, a solid purge is performed in the calciner depending on the fresh $CaCO_3$ feed. This purge consists mainly of CaO and $CaSO_4$.

Mass and energy balances to the CO_2 capture system described above for carbonation efficiencies (E_c) of 70, 80, and 90% have been solved. To solve these balances, the CaO in the carbonator is fixed between 1500 and 2000 kg/m^2, with a flue-gas flow rate of 6 m/s through the carbonator reactor, corresponding to an average solids residence time of 2 min depending on the solid circulation rates between reactors.

Figure 2 shows the results from these mass and energy balances, where every point on the curves would correspond to a given set of operating conditions in the CO_2 capture system. These operating conditions have been represented in terms of the fresh $CaCO_3$ make-up flow in the calciner (varying between 0.2 and 0.8 tonne of $CaCO_3$/tonne of coal in the whole system–existing power plant plus capture system) and the ratio between the chemical energy introduced with the coal in the calciner and in the whole system [$H_{cal}/(H_{cal} + H_{comb})$]. The solid circulation rate between reactors has been adjusted to maintain the desired carbonation efficiency (E_c). The ratio $H_{cal}/(H_{cal} + H_{comb})$ has been calculated considering the chemical energy based on the lower-heating value of the coal.

It can be observed that there is a minimum consumption of coal in the calciner corresponding to a minimum calciner size that sets the limit between sorbent activity maintained with high-$CaCO_3$ make-up flow or with high-solid circulation rates between reactors. These coal and $CaCO_3$ consumptions allow different strategies of design and operation, depending on the parameter to be optimized: the calciner
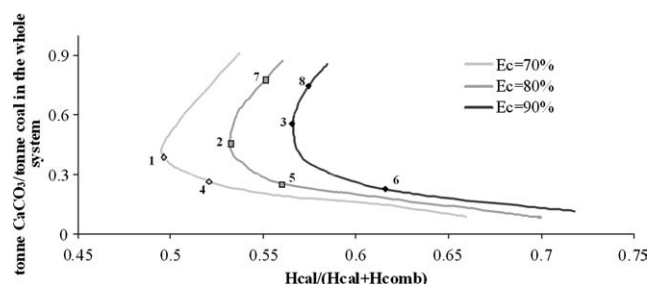
Figure 2. Energy fraction consumption in the calciner $[H_{cal}/(H_{cal} + H_{comb})]$ as a function of fresh $CaCO_3$ make-up flow and carbonation efficiencies (E_c) in the Ca looping system.

size or the fresh sorbent consumption. Three sets of operating conditions have been chosen for every carbonation efficiencies in Figure 2 to be integrated with the new supercritical steam cycle explained below. Specifically, those corresponding to the minimum calciner size (points 1, 2, and 3 in Figure 2) and two different settings corresponding to low-consumption of fresh $CaCO_3$ ($F_0/F_{CO_2} = 0.10$; points 4, 5, and 6 in Figure 2) and high-$CaCO_3$ consumption conditions ($F_0/F_{CO_2} = 0.35$; points 7 and 8 in Figure 2). The operation conditions selected will yield different energy availability distributions in the capture system that will determine the way to optimize the energy integration with the new supercritical steam cycle.

Thermal integration

As the Ca looping cycle works at high-temperature, it is possible to recover most of the energy of the gas and solids streams to produce superheated steam at 600°C and 28,000 kPa and generate additional power in a new supercritical steam cycle. Part of this additional power can be used to drive the air separation unit and the CO_2 compressor and, thereby, reduce the energy penalty caused by the capture process. The new steam turbine is comprised of two high-pressure bodies, two intermediate pressure bodies, a low-pressure body with five stages, and an auxiliary turbine to provide the energy for the cycle main pump. The detailed operating conditions of the steam turbine have been adopted from Romeo et al.[19] The heat requirements in the steam cycle are located in six zones depending on the temperature range: economizer, steam generator, superheater, reheater, and high-pressure and low-pressure water heaters. In a conventional system, all the energy that has to be transferred to the steam side in this equipment is generated in the boiler. However, because of the intrinsic characteristics of the Ca looping cycle, the conventional arrangement for energy recovery should be substituted by dispersed heat recovery systems. Therefore, significant differences were introduced with respect to conventional steam cycles. For example, to recover most of the energy available in the capture system, the economizer was separated into two stages (high- and low-temperature stages), and the steam bleeds, which feed the water heaters, were closed whenever possible. 600°C is the highest temperature of the steam cycle and is found in the superheater and the reheater where steam is heated

from 415°C and from 325°C, respectively. The economizer heats the water from 280 to 400°C, and the steam generator operates at temperatures between 400 and 415°C.

The energy sources in the Ca looping system that can be integrated with the supercritical steam cycle are the following:

(1) The concentrated CO_2 stream that leaves the calciner at 950°C, which can be cooled down to 150°C before being split.

(2) The energy that can be recovered in the carbonator as a result of the carbonation reaction and the cooling of the solids coming from the calciner at 950°C.

(3) The gas with a low-CO_2 content that leaves the carbonator at 650°C, which can be cooled down to 100–120°C before being sent to the stack.

(4) The CO_2 stream that goes to the purification and compression stages, which can be cooled down to 80°C before the water condensation stage.

(5) The solid purge from the calciner at 950°C, which can be cooled down before disposal or use as cement precursor.

The aim of all energy integrations proposed in this work has been to maximize the steam generation for the purpose of maintaining a temperature of 600°C for the steam side in the superheater and reheater. Heats recovered from the CO_2-rich stream in the calciner and from the carbonator represent the main energy inputs for the steam cycle. Both energy streams are suitable to be integrated into the superheater and reheater owing to their high-temperature energy availability. The energy requirements in the superheater exceeded, in almost all the simulated cases, the energy available in the carbonator. Therefore, the configuration that this work proposes consists of introducing in the superheater the energy available in the CO_2-rich stream ($Q_{rich\ CO_2}$), according to heat exchanger temperature levels. Then, the energy from the carbonator ($Q_{carbonator}$) will be split for introduction into the one-through steam generator (boiler) and into the reheater. The energy share-out between these two pieces of equipment will lead to a certain amount of steam in the cycle. So, if 600°C is maintained in the reheater, the steam in the cycle will be maximized to gain as much efficiency as possible.

The remaining energy still available in the CO_2-rich stream (after its integration with the superheater) will be used in the high-temperature stage in the economizer. Energy in the gas leaving the carbonator at 650°C ($Q_{clean\ gas}$) is integrated in the low-temperature stage into the economizer, where it is cooled down to 300°C. The outlet temperature of the clean gas in the first economizer will be always the same to maintain 20°C difference between the temperature of this stream and the temperature of the water incoming, the economizer. Therefore, the steam generated in the boiler will determine the energy needed in the second stage in the economizer and the temperature level for the remaining energy streams.

Figure 3 shows the basic thermal integration proposed for the CO_2 capture system with the new supercritical steam cycle. This basic energy integration was applied in all the selected operating conditions and was modified as needed according to the energy availability in the capture system. In some cases, it was necessary to implement a second superheater or second boiler, as will be explained in the simulation results.
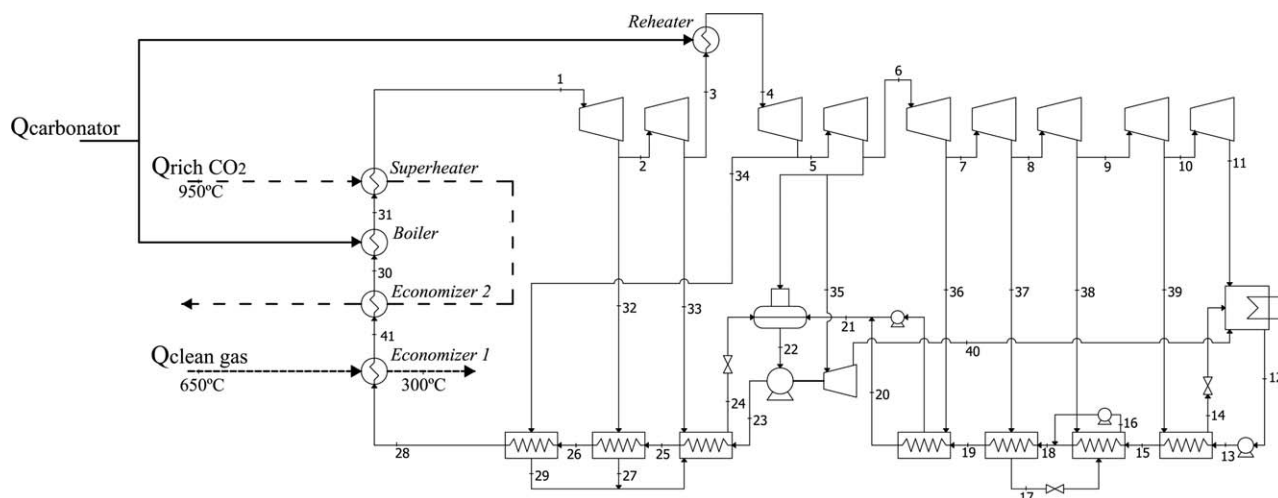
Figure 3. Reference thermal integration between the Ca looping system and the supercritical steam cycle (Cases 2, 3, and 4 from Figure 2).

Once the main energy fluxes are integrated following the layout represented in Figure 3, the number of turbine steam bleeds is reduced by using the residual energy remaining in the CO_2 capture system. There will be low-temperature energy available in the CO_2-rich stream, the CO_2-rich stream to purification, in the clean gas stream and in the solids purge. Depending on this energy availability, the number of steam bleeds in the steam turbine can be reduced.

Simulation results

The thermal integration strategy described above was applied to the selected operating conditions. The steam flow was maximized to maintain as high-efficiency as possible. To achieve this objective, it was necessary to introduce modifications in some cases with respect to the baseline integration proposed in Figure 3.

Although energy availability is different depending on the established carbonation efficiency and operation conditions, it should be highlighted that the energy in the CO_2-rich stream ($Q_{\text{rich } CO_2}$ in Figure 3) remains between 35 and 37% of the total energy input to the calciner in all of the condi-

tions studied. For identical values of capture efficiency, $Q_{\text{rich } CO_2}$ strongly depends on the $CaCO_3$ make-up flow owing to the additional CO_2 released during its calcination, and the CO_2 released from the additional coal used in the calciner to drive the calcination of the make-up flow.

On the other hand, the energy generated in the carbonator ($Q_{\text{carbonator}}$ in Figure 3) is between 20 and 35% of the energy input of the calciner, depending on carbonation efficiency and the flow of hot solids recirculated from the calciner. As carbonation efficiencies are always going to be high (between 70 to 90% in this work), solid circulation is the main variable determining the heat output from the carbonator. This solid flow is inversely proportional to the average activity of the sorbent material, which is in turn affected by the value of the limestone make-up flow. Therefore, low-make-up flow values translate into higher-solid circulation rates between reactors and higher-energy output in the carbonator. In these conditions, for the different cases studied in Figure 2, the $Q_{\text{rich } CO_2}/Q_{\text{carbonator}}$ can be between 1.6 and 1.9 for high-make-up flows from limestone and only ~1.0 when low-make-up flows are used in the system. These ratios have been found to have great influence on the final thermal
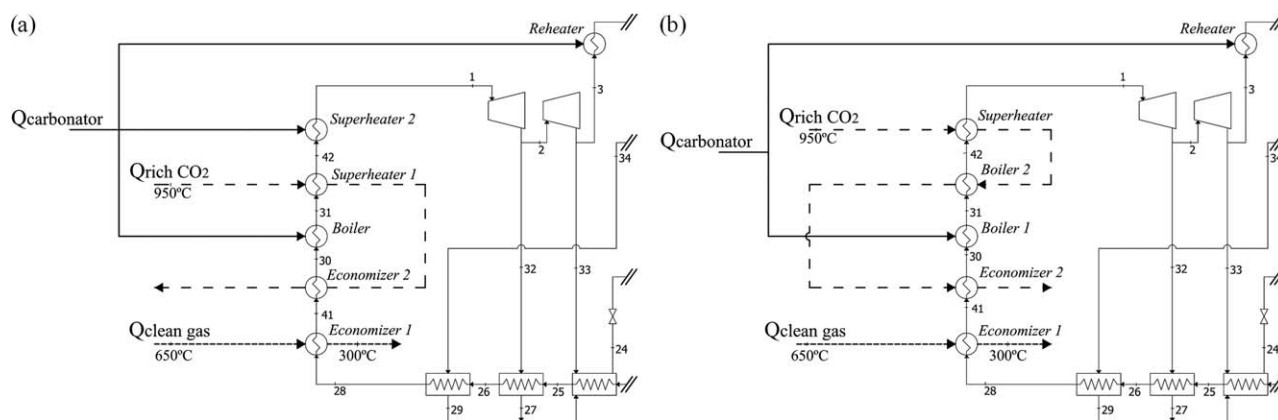

Figure 4. Detail of the thermal integrations proposed: (a) for the Cases 5 and 6 in Figure 2; (b) for the Cases 1, 7, and 8 in Figure 2.
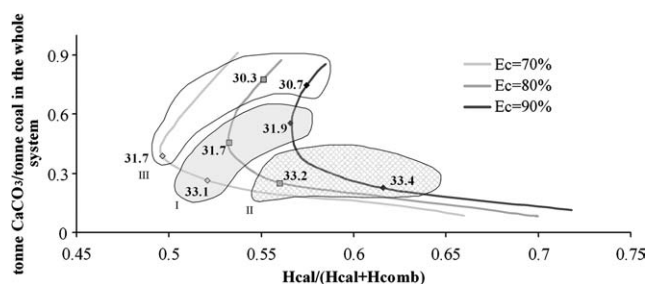
Figure 5. Diagram of the areas of application of the thermal integrations proposed as a function of the operational conditions of the Ca looping system. η_{net} for the simulation cases are included.

energy integration between the energy sources of the CO_2 capture system and the new supercritical steam cycle.

When this ratio is in the range of 1.4–1.8, no changes are needed in the reference thermal integration scheme adopted (Figure 3). Points 2, 3, and 4 represented in Figure 2 correspond to this baseline integration scheme.

Values of the ratio $Q_{rich\ CO_2}/Q_{carbonator}$ between 1.0 and 1.2 represent higher-energy disposal in the carbonator with respect to the CO_2-rich stream, because of either higher-solid circulation rates between reactors or higher-carbonation efficiency. The energy required in the superheater (supplied by the $Q_{rich\ CO_2}$) is four times the energy required in the boiler. Therefore, the CO_2-rich stream limits the energy from the carbonator that can be integrated in the boiler. In this way, once the baseline thermal integration has been implemented, energy excess remains in the carbonator and the steam flow can be increased by implementing a second superheater, as it can be seen in Figure 4a. This thermal integration corresponds to points 5 and 6 in Figure 2.

Values of the ratio $Q_{rich\ CO_2}/Q_{carbonator}$ higher than 1.8 imply that the excess energy in the CO_2-rich stream is so high with respect to the energy in the carbonator that, when applying the baseline thermal integration from Figure 3, there is an important energy excess in this stream. Points 1,

7, and 8 represent this situation. In these cases, this energy excess in the CO_2-rich stream is used to generate additional steam in a second steam generator according to Figure 4b.

In Figure 5, different zones (I, II, and III) are represented that show the limits of applicability for the different thermal integrations proposed, according to the ratio $Q_{rich\ CO_2}/Q_{carbonator}$. In short, it can be observed that there is a link between the energy available in the capture system, as a function of its operating conditions, and the optimum thermal integration corresponding to the highest-thermal efficiency.

Additional power is generated as a result of thermal integration between the CO_2 capture plant and the supercritical steam cycle. The gross power output of the system comprising the existing power plant and the Ca looping system was calculated according to Eq. 1

$$\eta_{gross} = \frac{W_{existing\ plant} + W_{supercritical\ cycle}}{H_{cal} + H_{comb}} \qquad (1)$$

$W_{existing\ plant}$ and $W_{supercritical\ cycle}$ are the net power output of the subcritical steam cycle and the new supercritical steam cycle, (accounting the energy consumption of the forced draft fans of the Ca looping cycle), respectively. An efficiency of 100% has been assumed for electricity conversion. H_{cal} and H_{comb} represent the chemical energy introduced in the whole system.

The main energy penalty associated with the CO_2 capture system, once the energy sources are integrated in the steam cycle, is the energy required to drive the calcination of the fresh sorbent. As mentioned in the process description section, the spent sorbent purged in this process could be used in the cement industry as raw material for clinker manufacture. In this case, the energy associated with the calcination of the $CaCO_3$ in this purged material would be saved. These savings, H_{calF_0}, (calculated as the product of the calcium molar flow in the purge and the calcination energy) should be discounted from the chemical energy introduced in the whole system. This results in an improved gross thermal efficiency $\eta_{i\text{-}gross}$, calculated by means of Eq. 2, which is compiled in Table 2.

Table 2. Thermal Efficiencies, Energy Penalties, and Main Consumptions in the Simulation Cases from Figure 2

Case in Figure 2	$\eta_{i\text{-}gross}$ (%) (Eq. 2)	W_{ASU} (MW$_e$)	$W_{CO_2\ compressor}$ (MW$_e$)	η_{net} (%) (Eq. 3)	η_{ref} (%) (Eq. 4)	Penalties Cement Synergy (% p.)
E_c 70%						
4—0.26 t of $CaCO_3$ make-up flow/t of coal	40.1	50	66	33.1	40.6	7.5
1—0.38 t of $CaCO_3$ make-up flow/t of coal	38.5	46	63	31.7	40.4	8.7
E_c 80%						
5—0.25 t of $CaCO_3$ make-up flow/t of coal	40.8	59	75	33.2	40.9	7.7
2—0.45 t of $CaCO_3$ make-up flow/t of coal	39.1	53	74	31.7	40.7	9.0
7—0.78 t of $CaCO_3$ make-up flow/t of coal	38.3	57	83	30.3	40.9	10.6
E_c 90%						
6—0.23 t of $CaCO_3$ make-up flow/t of coal	41.5	74	90	33.4	41.4	8.0
3—0.55 t of $CaCO_3$ make-up flow/t of coal	39.9	61	85	31.9	41.0	9.1
8—0.75 t of $CaCO_3$ make-up flow/t of coal	39.1	63	90	30.7	41.1	10.4

$$\eta_{i-\text{gross}} = \frac{W_{\text{existing plant}} + W_{\text{supercritical cycle}}}{H_{\text{cal}} + H_{\text{comb}} - H_{\text{cal}F_0}} \qquad (2)$$

The highest thermal efficiencies were obtained for the cases with lowest make-up flow, points 4, 5, and 6 in Figure 2. In these cases, where the modest activity of the sorbent is compensated by high-solids flow between reactors to maintain the desired carbonation efficiency (E_c), heat recovery from the gas and solids streams was more efficient. Differences in thermal efficiencies for the simulation cases are related with penalties associated with the energy in the streams leaving the capture cycle that cannot be further integrated in the steam cycle owing to either low-temperature or low-flow. These penalties will take place mainly in the CO_2 stream that goes to purification, the low-CO_2 content gas that goes to the stack and in the purge.

To calculate the net thermal efficiency of the system comprised of the existing power plant and the Ca looping system integrated with a new supercritical steam cycle, it is necessary to include the energy consumed by the air separation unit, W_{ASU}, considering a specific energy consumption of 160 kWh/tonne O_2;[25] the energy consumed by the CO_2 compressor stage, $W_{CO_2\text{ compressor}}$, considering a specific energy consumption of 100 kWh/tonne CO_2[25] and the usual power plant auxiliaries, $W_{\text{auxiliaries}}$, (5% of the gross power output of the new supercritical steam cycle[19]) and new fans needed for solids circulation. This is calculated according to Eq. 3.

$$\eta_{\text{net}} = \frac{W_{\text{existing plant}} + W_{\text{supercritical cycle}} - W_{\text{ASU}} - W_{CO_2\text{ compressor}} - W_{\text{auxiliaries}}}{H_{\text{cal}} + H_{\text{comb}} - H_{\text{cal}F_0}} \qquad (3)$$

The net thermal efficiencies of the simulation cases (included in Table 2) oscillate between 30.3 and 33.4%. These thermal efficiencies were calculated with state of the art major pieces of equipment such as the ASU or the CO_2 compressor, which are common in other CO_2 capture systems (like oxy-fired systems). Any future improvements in their energy consumption will also improve the efficiencies claimed in this work. In particular, it should be highlighted that the Ca looping system described in this article will benefit the fast development that is expected for oxy-CFB technology,[26] which is an enabling technology for the Ca looping process described in this work.

Simulation cases with the highest $CaCO_3$ make-up flow and low-circulation between reactors yield the lowest thermal efficiency ($\sim$30% for every E_c). As can be observed, low-$CaCO_3$ make-up flow values maximize the net thermal efficiency of the system, which is $\sim$33.2%. These maximums are related with the higher-heat recovery from the gas and solid streams that maximize the net power output (range from 445 to 678 MW) when integrated in the new supercritical steam cycle.

Optimum capture system operating conditions from the point of view of thermal efficiency would comprise a $CaCO_3$ make-up flow between that required for minimum calciner size conditions (representing $\sim$6% of purge material in weight of the solids circulating to the carbonator) and the minimum $CaCO_3$ make-up flow in this work ($F_0/F_{CO_2} = 0.1$, representing a purge stream between 1 and 2% in weight of the solids circulating to the carbonator). These results are in agreement with Romeo et al.[20] who recommended avoiding operating conditions with low-recirculation rates and purge percentages over 5% to optimize the cost per tonne of CO_2 avoided. That work concludes that minimum tonne CO_2 avoided cost is achieved when a molar CaO/CO_2 ratio of 5 and a purge percentage of 1.5% are chosen. Further reductions in the $CaCO_3$ make-up flow in the system (see curves in Figure 2) will significantly increase coal needs in the calciner, resulting in higher ASU and CO_2 compression consumption that would negatively affect the thermal efficiency obtained. Purge streams representing the 1–2% or as high as 5% of the solids from the calciner are still competitive in terms of CO_2 avoided cost for Ca looping systems based on natural sorbents. The use of more expensive synthetic sorbents reduce the optimum purged material well below 1%.[27] In this case, the amount of inert material in the Ca looping system (ash and deactivated sorbent) would dramatically increase the energy requirements in the calciner when introducing coal to drive sorbent calcination.

ASU and CO_2 compression energy consumption are compiled in Table 2. Simulation cases corresponding to minimum calciner size always represent the lowest energy requirements in the ASU and in the CO_2 compressor. High-$CaCO_3$ make-up flow results in higher-compression consumption, especially when compared between operating conditions that require a similar amount of coal introduced in the calciner (Cases 5 and 7 in Figure 2). On the other hand, the cases with the lowest $CaCO_3$ make-up flow require the highest coal consumption for a given CO_2 capture efficiency, and, therefore, present the highest ASU consumption. To put these consumptions levels into context with other CO_2 capture technologies that also require an ASU as oxy-combustion technologies, it should be pointed out that a stand-alone oxy-fired power plant aiming to avoid the amount of CO_2 coming from both, the existing power plant and the CFB-calciner would require almost double ASU consumption.

Under the above defined operating conditions, two different operation strategies can be followed to optimize the thermal efficiency of the system. The CO_2 capture system can be designed to operate close to minimum calciner size; this requires an ASU providing O_2 from 286 to 378 tonnes/h. Under those conditions, solid inventory in the carbonator would be $\sim$1500 kg/m^2 and solid circulation rates between 6.5 and 7.6 kg/m^2 s. On the other hand, the system could be designed to operate with a low-$CaCO_3$ make-up flow that would require oxygen production between 316 to 466 tonnes O_2/h. Solids inventory in the carbonator would be $\sim$1700 kg/m^2 and the solid circulation rate (entering the carbonator) would be between 9.3 and 16.8 kg/m^2·s as the carbonation efficiency increases.

To evaluate energy penalties associated with the capture system, a reference plant consisting of the existing subcritical power station and a new hypothetical supercritical power plant with the same fuel input as the calciner is considered. It is assumed that the efficiency for the subcritical plant is

36%, for the supercritical plant is 45%,[19] and the combined efficiency of the whole system is calculated according to Eq. 4. The results obtained for the reference efficiency are compiled in Table 2.

$$\eta_{ref}(\%) = \frac{H_{cal}}{H_{cal} + H_{comb}} \times 45 + \frac{H_{comb}}{H_{cal} + H_{comb}} \times 36 \quad (4)$$

Therefore, the energy penalties with respect to the reference plant considered, show values of ~7.5% p. for minimum $CaCO_3$ make-up flow and around 9% p. for minimum calciner size conditions. These penalties were obtained considering the integration of the system with a cement production plant. If this integration does not take place, the efficiency penalties increase and the range oscillates between 8.3 and 10.3% p.

The discussion in this article is based on a subcritical reference plant. However, as the only link between the existing plant and the Ca-looping system is the flue-gas stream, the same thermal integration proposed would apply to a reference system based on a supercritical power plant consuming the same amount of coal but generating power with a 45% net efficiency. In this case, the η_{ref} in Eq. 4 for the whole system would be also 45% and η_{net} from Eq. 3 would be comprised between 34.6 and 36.9%.

Conclusions

The energy sources from a calcium looping system (understood as energy in the gas and solid streams leaving the system) can be integrated into a supercritical steam cycle to produce additional power output. The thermal integration of these energy sources with the equipments in the steam cycle is strongly linked with the operating conditions of the capture system. It has been observed that the energy contained in the gas stream leaving the calciner ($Q_{rich\ CO_2}$) represents a rather constant fraction of the total energy introduced into the Ca looping system (between 35 and 37% of H_{cal}). On the other hand, the energy available in the carbonation unit strongly depends on the operating conditions of the capture system (from 20 to 35% of H_{cal}). The ratio between these two energy streams $Q_{rich\ CO_2}/Q_{carb}$ has been found to be very important for determining the thermal integration of the Ca looping system and the steam cycle. Operating conditions that present the ratio between 1.4 and 1.8 (corresponding to minimum calciner size) integrate the $Q_{rich\ CO_2}$ with the superheater and $Q_{carbonator}$ is shared out between the boiler and reheater. High-$CaCO_3$ make-up flow conditions (ratio $Q_{rich\ CO_2}/Q_{carb}$ over 1.8) present an excess CO_2-rich stream with respect to the energy in the carbonator. This energy excess is integrated with a second boiler. Finally, low-$CaCO_3$ make-up flow conditions results in ratios $Q_{rich\ CO_2}/Q_{carb}$ between 1.0 and 1.2. In these cases, the energy in the carbonator exceeds the energy in the CO_2 stream and a second reheater is implemented with respect to the baseline case.

The thermal efficiency of the system comprising the existing power plant and the Ca looping system integrated with a new supercritical steam cycle has been calculated. The results obtained show that heat recovery from gas and solids streams is more efficient for the cases with the lowest $CaCO_3$ make-up flow. The net thermal efficiencies of the simulated cases range between 30.3 and 33.4% when the synergy between the Ca looping system and a cement plant is considered. With state of the art components, efficiency penalties can be as low as 7.5% p. of net efficiency with respect to the defined reference plant when working with low-$CaCO_3$ make-up flows. Operating conditions close to minimum calciner size result in slightly higher penalties of ~9% p. A major source of the penalty in this Ca looping system is the energy consumption of the ASU required to operate the calciner. This is, however, about half the size of the ASU of an equivalent stand-alone oxy-fired system. Any improvement on O_2 generation or CO_2 compression technologies will also directly benefit the efficiencies of the calcium looping system described in this work.

Acknowledgments

Notation

E_c = CO_2 capture efficiency in the carbonator
F_0 = fresh $CaCO_3$ molar make-up flow, mol/s
F_{CO_2} = CO_2 molar flow entering the carbonation reactor, mol/s
F_{CaO} = CaO molar flow circulating between calciner and carbonator, mol/s
H_{cal} = chemical energy introduced with the coal (based on coal lower-heating value) in the calciner unit, MW
H_{calF_0} = chemical energy associated with the calcination of the calcium in the solid purge, MW
H_{comb} = chemical energy introduced with the coal (based on coal lower-heating value) in the reference plant, MW
$Q_{carbonator}$ = energy available in the carbonator, MW
$Q_{clean\ gas}$ = energy available in the gas stream from the carbonator, MW
$Q_{rich\ CO_2}$ = energy available in the rich CO_2 gas stream from the calciner, MW
$W_{existing\ plant}$ = net power output of the subcritical steam cycle steam cycle, MW
$W_{supercritical\ cycle}$ = net power output of the new supercritical steam cycle understood as MW produced in the steam turbines minus pumps and fans consumptions
W_{ASU} = ASU energy consumption, MW
$W_{auxiliaries}$ = auxiliaries energy consumption, MW
$W_{CO_2\ compressor}$ = compressor energy consumption, MW

Greek letters

η = thermal efficiency
gross = gross thermal efficiency (according to Eq. 1)
i-gross = improved gross thermal efficiency (according to Eq. 2)
net = net thermal efficiency (according to Eq. 3)
ref = thermal efficiency of the reference plant (according to Eq. 4)

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