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Optimizing make-up flow in a CO_2 capture system using CaO

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ABSTRACT

CO_2 capture system based on the carbonation/calcination loop, still in its infancy, has gained rapid interest due to promising carbonator CO_2 capture efficiency, low sorbent cost and the fact that no flue gases desulphurization unit is needed before entering the system. The sum of these features results in a competitively low cost CO_2 capture system. There are different options to design the carbonation loop. In this work, a basic configuration that makes use of two interconnected circulating fluidized beds (carbonator and calciner) has been studied. Among the key variables that influence the performance of these systems, the carbonation conversion of the sorbent and the heat requirement at calciner are the most relevant. Both variables are mainly influenced by CaO/CO_2 ratio and make-up flow (purge) of solids. A purge is necessary in order to reduce the sorbent deactivation and to compensate the formation of $CaSO_4$ from the SO_x content in the flue gas. Large CaO/CO_2 ratios improve the carbonation conversion but also increase the cost of the system due to a more intensive solid circulation. High make-up flow also improves the carbonation conversion and hence the CO_2 capture, but increases the heat demand at calciner and the fresh sorbent cost. The aim of this paper is to calculate the optimum make-up flow and CaO/CO_2 ratio in order to minimize the capture cost of the system. Independent variables are make-up flow of fresh $CaCO_3$ and CaO/CO_2 ratio. The constraint equations are experimental data on carbonation reaction, mass and energy balances, oxygen requirement and fuel composition.

1. Introduction

IPCC has pointed out capture of CO_2 from large stationary sources as a feasible mid-term mitigation option for climate change [1]. Recent researches suggest that one of the most promising processes for in situ CO_2 separation relies on the use of the chemical equilibrium of some Ca-based sorbents, widely available and very cheap, via the following gas–solid reaction, carbonation, Eq. (1) [2–9].

$$CaO(s) + CO_2(g) \leftrightarrow CaCO_3 \qquad (1)$$

Under specific operating conditions (pressure and temperature), the relationship between the equilibrium CO_2 concentration in the gas after CO_2 capture can be obtained from the equilibrium constant expression [10], shown below Eq (2):

$$\log_{10} P_{CO_2} = 7.079 - \frac{8308}{T} \qquad (2)$$

The analysed system consists of two interconnected circulating fluidized bed, i.e. a carbonation reactor and a calcination reactor, creating an almost closed loop for the CO_2 carrier (Fig. 1). The carbonator receives a stream of flue gases from an existing power plant and the CO_2 will react with CaO to form $CaCO_3$. Sorbent regeneration takes place in the second CFB where $CaCO_3$ is calcined producing a concentrated stream of CO_2 suitable for capture/compression. Heat requirements for sorbent calcination are covered by oxyfuel combustion of coal in the second reactor itself.

One critical aspect for processes involving Ca-based sorbents deals with conversion efficiency of carbonation reaction under process conditions and its variation after several cycles [11–13]. Deactivation of the sorbent carbonation activity with an increasing number of cycles is a key parameter which influences on both cost and heat requirements. To compensate for these losses in sorbent activity, a make-up flow of fresh $CaCO_3$ is introduced in the calciner and a controlled solid purge flow will counterbalance the mass balance in the reactor.

It is assumed that calcination will be fast and complete under operation conditions in this reactor. However, several experimental studies [8,14] showed the carbonation reaction is far from reversibility. There are two major limiting factors in CO_2 capture efficiency: equilibrium partial pressure of CO_2 dictated by Eq. (1) and reactor design which determines gas–solid contact and residence time [5]. Equilibrium permits capture efficiencies of around 95% for typical flue gases concentrations of CO_2 under process

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Nomenclature

b	fitting parameters in Eqs. (4) and (5)
CFB	circulating fluidized bed
COE	cost of electricity
f	fitting parameters in Eqs. (4) and (5)
f_p	percentage of purged solid
F_{CO_2}	molar flow of CO_2 produced by combustion in the reference plant
F_{gas}	molar flow of flue gases from the reference plant excluding CO_2
HPT	high-pressure turbine
ΔH°_{R1}	heat of reaction for the carbonation–calcination equilibrium
IPCC	intergovernmental panel on climate change
LHV	low heating value
LPT	low-pressure turbine
MPT	medium-pressure turbine
P_{CO_2}	CO_2 partial pressure
Q_{calc}	recoverable heat from calcination reactor
Q_{carb}	recoverable heat from carbonation reactor
Q_{comp}	recoverable heat from CO_2 compression train
R	CaO/CO_2 molar ratio
X_{ave}	maximum average capture capacity of CaO
y_{comb}	fuel fraction to combustor

Greek letters

η_{capt}	CO_2 capture efficiency

Subscripts

capture	reference plant + capture system
CL	calcinator
CR	carbonator
ref	reference plant

conditions, 650 °C and atmospheric pressure. Reactor design limitations might lead to capture efficiency decays to lower values.

Carbonation conversion is enhanced by both large CaO/CO_2 ratios and make-up flows of solids. However, high CaO/CO_2 ratios increase the cost of the system due to intensive solid circulation and the higher make-up flow, the more significant heat demand at calciner and the larger cost of fresh sorbent [6].

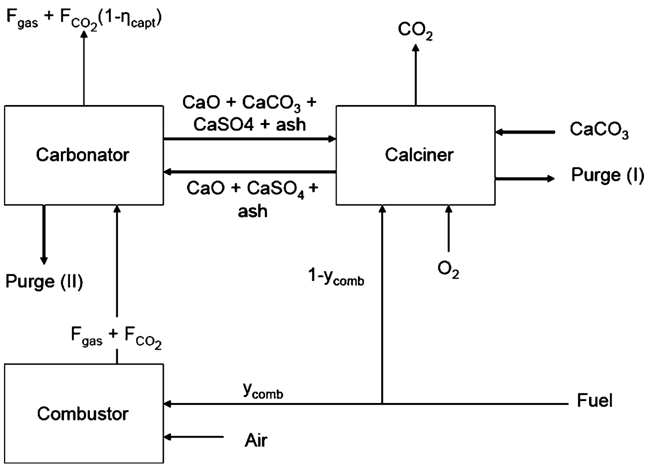

Fig. 1. Carbonation/calcination loop flowsheet.

In the following, a comprehensive study optimizing the energetic performance and economics of CO_2 capture and sequestration technologies applied to an existing coal-fired electric generation power plant is presented. The purpose of this study is to assess the influence of solids purge flows percentage in both reactors on the total costs of electricity and the cost of captured tCO_2. Mass and energy balances in the system are solved and obtained results used as input data in the economical model.

2. Overall system description and simulation

The basic concept of the overall system is to apply carbonation/calcination CO_2 capture technology to clean flue gases from an existing power plant and integrate released heat flows from capture and compression processes into a new supercritical steam cycle which generates extra electrical power. The new concept has been evaluated against a baseline case from the point of view of performance and impacts on power generating cost. The reference power plant generates 500 MWe and the net efficiency of the unit is 40.32% LHV. It has been supposed for calculations a high-rank coal (66% C, 8% H_2O, 13% ashes, 25.3 MJ/kg) whose sulphur content remains below 0.65% dry basis. Flue gases flow of the reference power plant, 546.80 kg/s, 21.72 wt% CO_2 is fed to the carbonator loop.

2.1. CO_2 capture plant

Fig. 1 illustrates the CO_2 capture process in post-combustion using a carbonation–calcination loop. The flue gases from the existing power plant ($F_{gas} + F_{CO_2}$) are sent to the capture system. In the carbonation CFB reactor, reaction (1) takes place and its extent (defined as CO_2 capture efficiency, η_{capt}) is shown in Eq. (3), where X_{ave} is the maximum average capture capacity of CaO within the loop and R is the CaO/CO_2 molar ratio [3].

$$\eta_{capt} = RX_{ave} \tag{3}$$

The expression of X_{ave} for the circulating lime is a function of the percentage of purged solid, f_p, and the location of the purge. When purge is extracted from calcination reactor, Eq. (4) is used and the values for f and b parameters are 0.77 and 0.17, respectively [3]. However, if fresh limestone inlet flow is counterbalanced purging at the bottom of carbonation reactor, Eq. (5) is applied in X_{ave} calculation and the values of these fitting parameters are 0.782 and 0.174 [2].

$$X_{ave,CL} = \left[\frac{f(1-b)f_p}{f_p+1-f}+b\right] \tag{4}$$

$$X_{ave,CR} = \left[\frac{ff_p}{f_p+1-f}+b\right] \tag{5}$$

The required stream of calcined lime depends on both the CO_2 in the flue gases and the CaO/CO_2 molar ratio, R, chosen for operation. The temperature of carbonator CFB operation must be set around 650–670 °C [10]. The extra heat released by the carbonation exothermic reaction ($\Delta H^\circ_{R1} = 168.5$ kJ/mol) and the heat extracted from clean gases leaving the carbonator at high temperature will be allocated in the new steam cycle, Q_{carb}.

Due to the extremely high Ca/S molar ratio in the carbonator, the reaction between all SO_x present in the flue gases and CaO is ensured. As a result, there is a percentage of $CaSO_4$ in the solid circulating within the loop. Previous studies [6,15,18] consider the deactivation of the sorbent by $CaSO_4$ formation assuming that sulphur reacts exclusively with the part of CaO which is active for carbonation. However, this assumption leads to an overly conserva-

Table 1
Main technical assumptions of the model

Technical assumptions for the system	
Carbonation/calcination system	
Purge final temperature (°C)	180
Carbonation final flue gases temperature (°C)	180
Calciner flue gases temperature before compression (°C)	53–59
CO_2 compression train	
Intercooling temperature at CO_2 compression (°C)	50
Pressure ratio at CO_2 compression	3.3
CO_2 recirculation (%)	17–21
ASU consumption (kWh/tO_2)	220
CO_2 properties after compression	80 °C, 120 bar
Supercritical steam cycle	
Power plant boiler flue gases temperature (°C)	180
Deaerator pressure (bar)	7
Condenser pressure (bar)	0.045
Live steam properties at turbine inlet	600 °C, 290 bar
Reheat steam properties at turbine inlet	620 °C, 48.5 bar

tive X_{ave} definition as stated in [16,17] and has not been considered in this work.

The solid stream leaving the carbonator is introduced into the calciner that operates at 900–930 °C to regenerate the sorbent. Both, the strongly endothermic calcination reaction which releases CO_2 and the heating up of the incoming solids from the carbonator up to the required temperature, demand large amounts of energy provided by coal oxyfuel combustion in a CFB reactor.

An air separation unit (ASU) is needed to provide oxygen for oxyfuel combustion. The required oxygen flow is ranged from 36 to 107 kg/s. Multiple trains of an air separation unit would have to be used to produce the demanded oxygen, an important auxiliary consumption is therefore needed to produce the required oxygen quantities (3200–9300 T/day). A typical value of 220 kWh/tonne O_2 has been taken for ASU power consumption [1].

Recirculation of flue gases from calciner is essential in oxyfuel combustor performance to provide enough gas velocity to reach CFB operation and to control bed temperature. The recirculation of the CO_2 concentrated gas ranges from 17 to 21% of the total outlet stream to ensure an inlet O_2 mass fraction in the gas flow of 30%.

To compensate conversion decay of CaO and sorbent loss due to $CaSO_4$ formation, a purge of sorbent material is needed. The solid purge in the system has been defined as a percentage over the total mass flow leaving the reactor when no purge is considered. This output flow takes into account all inlet flows and the corresponding chemical reactions within each reactor. The composition of purge is different for each reactor (Fig. 1). A make-up flow of fresh sorbent is introduced into the system to counterbalance the purged calcium. The amount of solid purge and make-up flow influence the system performance. A large make-up flow improves carbonation conversion by reducing the average carbonation–calcination cycles of the solid material and increasing the carbonation efficiency, Eq. (3). However, significant amounts of purge dramatically increase the heat demand at calciner, the oxygen production cost and the auxiliaries consumption. The solid purge heat exchangers reheat both CO_2 recirculation to the calciner and O_2 entering the calciner.

2.2. CO_2 compression train

The compression train consists of four turbocompressors (isentropic efficiency 80%) connected in series. CO_2 enters the system at temperatures between 53 and 59 °C (Table 1), and atmospheric pressure. CO_2 compression turbine is operated by a steam extraction from the turbine MPT2 whose flow varies from 40.6 to 163.2 kg/s depending on the simulated case. Total compression energy required to CO_2 conditioning for transport, 120 bar and 80 °C, ranges from 32 to 130 MW which represents about 5–14% of the total energy output (reference plant plus new steam cycle). The compression process requires intercooling stages to reduce compression demands and to avoid excessive CO_2 temperature. A potentially recoverable low-temperature heat, Q_{comp}, is generated.

2.3. Steam cycle and heat integration

As represented in Fig. 2, the supercritical steam cycle (see Table 1 for steam properties) consists of a heat recovery steam generator (HRSG), high-pressure turbine, reheater, three medium-pressure turbines and one low-pressure turbine, condenser, low-pressure preheating system, deaerator, high-pressure feedwater heaters and economiser. No steam turbine bleeds are necessary for water preheating due to heat integration with CO_2 compression train and flue gases from calciner and carbonator used as high-pressure heaters. Steam cycle has been simulated through mass and energy balances for each equipment in the system. Turbines are defined by using isentropic efficiencies (89% for high-pressure turbine and 91% for the rest of them). High-pressure pump is operated by the MPT2 turbine extraction. Main technical assumptions considered for this simulation are gathered in Table 1. Steam mass flow production mainly depends on solid circulation in the CFB's so the design and extra power output vary depending on the same variables previously described (CaO/CO_2 molar ratio and purge percentage).

Recovered heats from carbonator, Q_{carb}, and calciner, Q_{calc}, are used to design the high-pressure equipments of a supercritical cycle (HRSG, re-boiler and high-pressure pre-heaters) according to the heat exchangers temperature levels. Heat recovery steam generators take advantage of the flue gases from carbonator at 650 °C and from calciner at 930 °C. A solid–gas heat exchanger is used to reduce the purge temperature from the corresponding temperature operation of the purged reactor down to 180 °C. Intercooling CO_2 compression heat, Q_{comp}, is used in low-pressure heat exchangers in the condensate section of the steam cycle.

2.4. Economic assessment

The final purpose of the study is to optimize the cost of avoided tCO_2, defined in Eq. (6), depending on sorbent make-up flow. This expression for the cost of avoided CO_2 takes into account the cost of reducing atmospheric CO_2 emissions while providing the same amount of product as the reference plant without CO_2 capture system [1].

$$\text{Cost avoided tCO}_2 = \frac{(\text{COE})_{\text{capture}} - (\text{COE})_{\text{ref}}}{(\text{CO}_2 \times \text{kWh}^{-1})_{\text{ref}} - (\text{CO}_2 \times \text{kWh}^{-1})_{\text{capture}}} \quad (6)$$

Reference plant and capture plant capital costs have been taken from literature [18]. Amortization costs, fixed costs, O&M costs, fuel costs and sorbent costs of the capture plant have been considered. The extra auxiliary consumption in the capture system is mainly generated by the ASU whose electrical consumption ranges broadly depending on the case under study. The main assumptions for these calculations are presented in Table 2, it has been supposed a capital investment of €1100 $\text{kW}_{\text{gross}}^{-1}$ for the reference power plant and a conservative value of €2070 $\text{kW}_{\text{gross}}^{-1}$ (€2383 $\text{kW}_{\text{net}}^{-1}$) according [19] for the capture system comprising an oxy-CFB calciner, a CFB carbonator and the steam cycle. The total investment is M€550 for the reference case with a cost of electricity (COE) of €31.9 MWh^{-1} and emission of 905.1 kgCO_2/MWh. These figures change for the different carbonation loop sizes obtained depending CaO/CO_2 molar ratio and purge percentage.

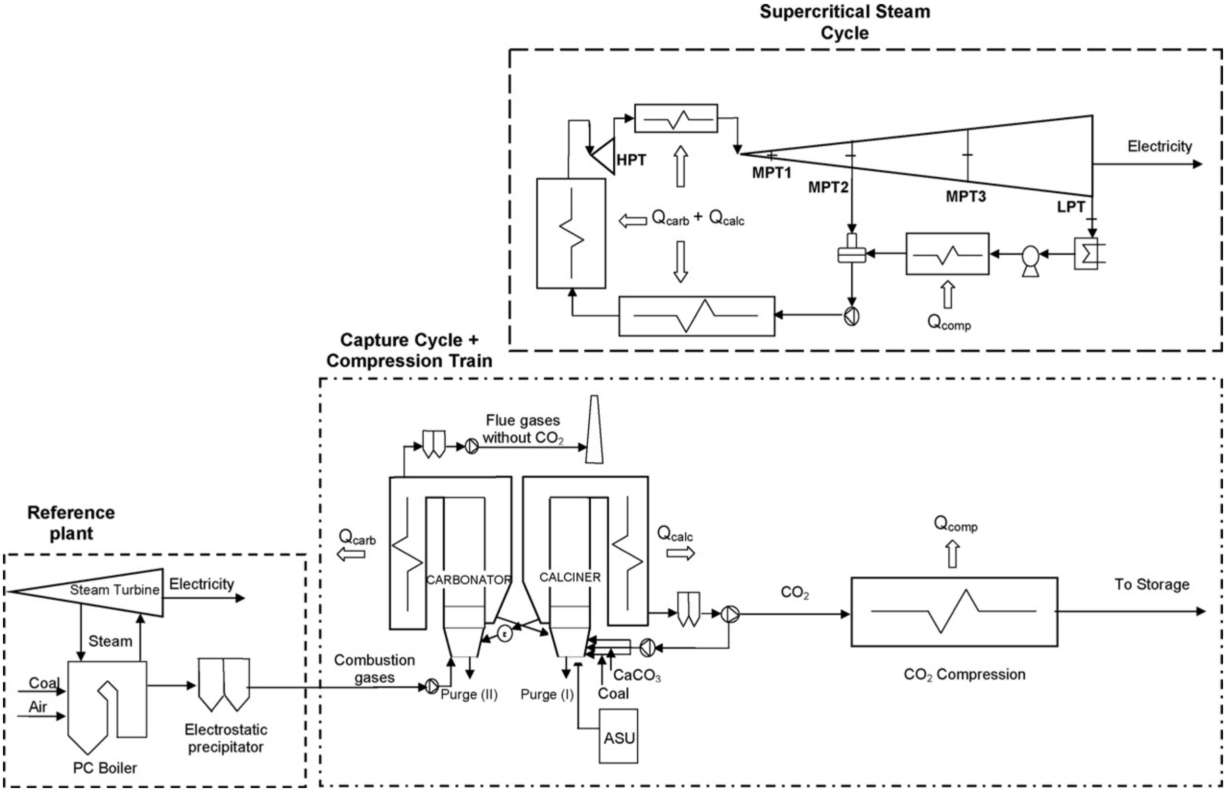

Fig. 2. Integration of residual heat streams from carbonation calcination loop into a steam cycle.

3. Results and discussion

Carbonation cycle has been simulated considering make-up flow as independent variable, the process has been integrated within the described steam cycle and with the aim to minimize the CO_2 avoided cost. Two possible cases have been studied depending on the location of purge, at carbonator or calciner.

The purge at carbonator is mainly composed of $CaCO_3$, although $CaSO_4$ and CaO are also present. At steady state, purge flow always compensates the $CaSO_4$ formation from SO_x content in flue gases, so the calcium sulphate in the loop increases with purge reductions. The same behaviour is observed with ashes from the coal fed into the calciner. Fig. 3 illustrates the solid mass flow at calciner inlet for Ca/CO_2 molar ratio of 4. The amounts of CaO and $CaCO_3$ remain unchanged for this molar ratio, ashes and $CaSO_4$ reduce when the purge increases. For a lower Ca/CO_2 molar ratio, the total mass flow of $CaSO_4$ and $CaCO_3$ remain constant. In this case, ashes content in the circulating flow is slightly reduced due to the less energy input, as coal, necessary for calcination. Finally, the molar ratio diminution leads to a strong reduction in CaO presence at carbonator and consequently a carbonation efficiency decrease as stated in Eq. (3). Fig. 4 shows the mass fraction of each component in the carbonator purge flow for a constant molar ratio of 4. Increasing purge flow, the CaO mass fraction in the carbonator increases and so does the $CaCO_3$ mass fraction as a result of improved carbonation efficiencies.

Fig. 5 shows the influence of the purge percentage from carbonator and the Ca/CO_2 molar ratio on the tCO_2 avoided cost for carbonator efficiencies given by Eq. (3). In general, this cost is well below €20/tCO_2 as previously reported elsewhere [19–21]. As can be seen, there is a different optimum value of the CO_2 avoided cost for each Ca/CO_2 molar ratio. This minimum cost corresponds to a specific purge percentage; larger values do not improve economical performance of the capture system based on $CaCO_3$. A higher make-up flow reduces the solid circulation for a given CaO/CO_2 ratio. Nevertheless this effect does not seem relevant compared to

Table 2
Economical assumptions for the installation

Main economical assumptions	
Interest rate (%)	8.78
Amortization period	25
Reference plant capital cost	€1100 $kWgross^{-1}$ (€1158 $kWnet^{-1}$)
Capture plant capital cost	€2070 $kWgross^{-1}$ (€2383 $kWnet^{-1}$)
Fixed costs	1%
O&M costs	2%
Fuel cost	€0.006 th^{-1} (€1.43 GJ^{-1})
Sorbent cost	€6 T^{-1}
Auxiliary consumption for reference plant	5% of gross power output
Auxiliary consumption for capture plant	5% of total gross power output + 28 – 85 MW (ASU)

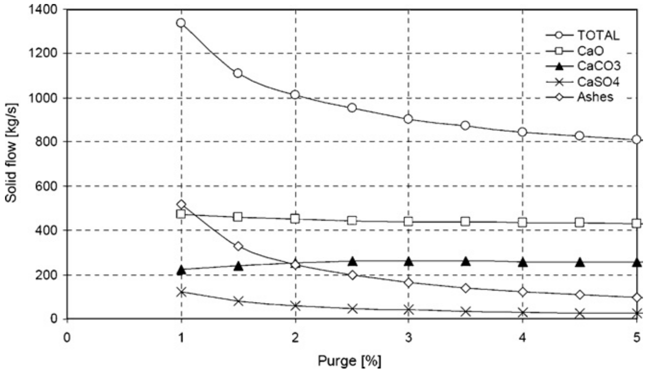

Fig. 3. Solid mass flow at calciner inlet for CaO/CO_2 molar ratio 4.

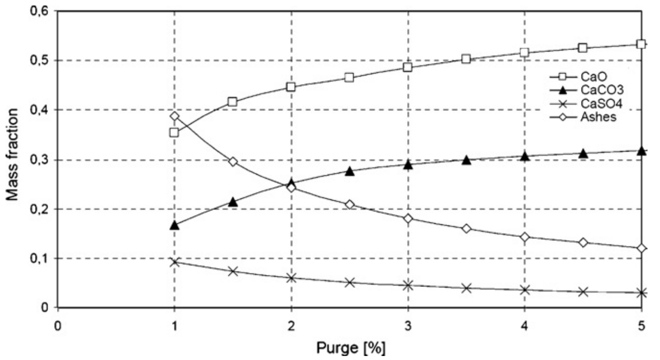

Fig. 4. Mass fraction of components at carbonator purge for CaO/CO_2 molar ratio 4.

both the increase in sorbent cost and the reduction of heat recovery from solid and gas streams. The higher CaO/CO_2 molar ratio, the more important purge influence on capture cost. The slope of these curves becomes softer for low solid flow circulating between both reactors. There is a sharp drop in purge influence (slope) when CaO/CO_2 ratio is reduced from 4 to 3. The explanation lies in the fact that capture efficiency reaches its maximum at a specific purge percentage which is different for every *R*. Increasing purge percentage over that limit do not increase CO_2 capture capacity. Nonetheless COE rises monotonically with purge. For a molar ratio of 3, the maximum capture efficiency is reached at purge values around 6% (over the maximum purge value represented in Figs. 3–6). Thus, a constant decreasing trend characterizes the CO_2 emissions within the range of purge percentage presented in the figures. This behaviour of the GHG's emissions compensates the permanent increase of COE when the make-up flow gets larger and, therefore, the resulting slope in Figs. 5 and 6 is smoother. Reducing to a ratio of 2, this influence does not significantly change. However for a molar ratio of 4, the maximum capture efficiency is reached at much lower purge values, around 2%, and, from this value up, CO_2 emissions remain constant. In this scenario, the constant gain in COE will not be counterbalanced and the resulting curve for tCO_2 avoided cost will follow the same trend as COE with a pronounced slope.

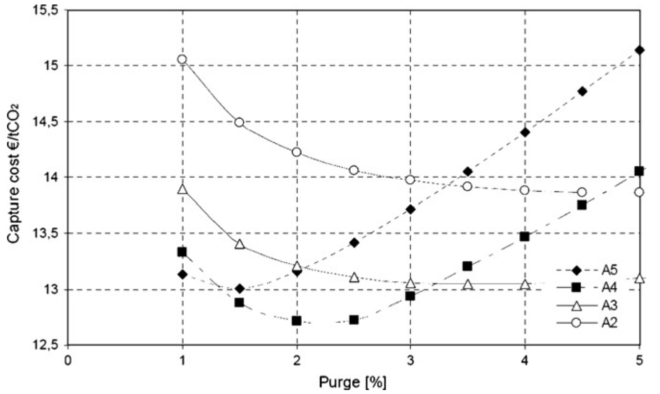

Fig. 5. CO_2 avoided cost at carbonator purge for different CaO/CO_2 molar ratio and purge percentage.

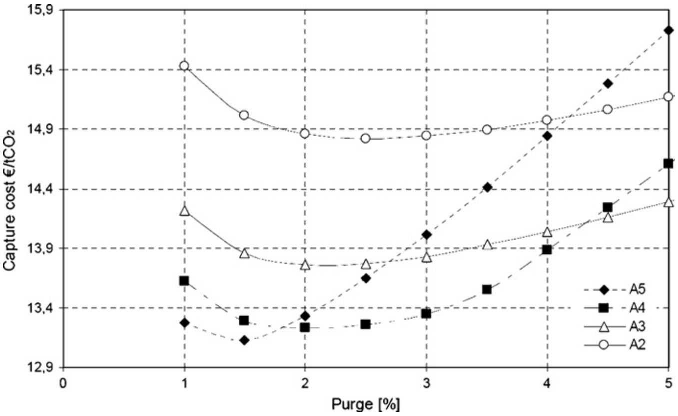

Fig. 6. CO_2 avoided cost at calciner purge for different CaO/CO_2 molar ratio and purge percentage.

Minimization of tCO_2 avoided cost is reached for high CaO/CO_2 molar ratios, about 4, and low purge percentage in carbonator, 2%. This minimum capture cost achieved under optimal conditions remains below €12.8/tCO_2. If make-up flow is reduced to values below 1%, the capture cost is optimized for a molar ratio of 5. These figures agree with previous conclusions stating that purge is not an essential factor when high solid amounts circulate in the loop. Under this condition, the residual activity of $CaCO_3$ is enough to attain a significant CO_2 capture [11]. When the purge percentage increases over 3.5, minimum cost is found for a CaO/CO_2 molar ratio of 3 and the optimum when 5% of solids is purged in the carbonator is obtained for molar ratio 2. It seems reasonably to design the system considering those operation conditions identified as the optimal ones: high CaO/CO_2 molar ratio, around 4, and purge percentage of 2% in order to maintain tCO_2 avoided cost approximately at €12.7/tCO_2. The process has a CO_2 capture efficiency of about 96% in the carbonator and 100% in oxyfuel combustion.

In the optimum scenario, the process needs high solid circulation between the circulating fluidized beds (CFB). In this case, the solid mass flow from carbonator to calciner is 1011 kg/s (44.5% CaO, 25.1% $CaCO_3$, 6.0% $CaSO_4$ and 24.4% ashes). This value increases up to 1338 kg/s with purge percentage of 1% and drops for higher purge values, 906 kg/s for 3% and 809 kg/s for 5% (Fig. 3). Higher make-up flows do not significantly reduce solid circulation, causing the U-shape of the curve in Fig. 5. The required solid circulation between calciner and carbonator may be easily obtained using two CFB. Supposing a solid flow of about 10 kg/m^{2}s, two CFB similar to those used for 150–200 MWe utilities are needed. This value agrees the extra power output generated after the integration of CO_2 capture loop into the reference power plant, 375.32 MW, as presented below.

Under the above defined optimum performance conditions, solid mass flow from calciner to carbonator is 917 kg/s, mainly composed of CaO. The inlet flows required to operate the capture process are 38.5 kg/s of coal, 22.5 kg/s of fresh $CaCO_3$ and 78.2 kg/s of oxygen. All of them are introduced into the calcination CFB reactor. Heat streams from carbonator, calciner and CO_2 compression are integrated into a new steam cycle producing an extra gross output of 375.32 MW. After taking into account the oxygen production and the auxiliaries of the new power plant and the capture system, the generated power becomes a net output of 288.7 MW. Total investment for the integrated system with a cost of electricity (COE) of €43.1 MWh^{-1} and CO_2 emissions of 4.8 kg/s, is considered to be M€1330. This economical data lead to a CO_2 capture cost of €12.7/tCO_2 as presented above.

Fig. 6 shows a similar trend in the results for the purge at calciner, mainly composed of CaO and $CaSO_4$. Results are in agreement with those previously presented in [6]. This outstanding study analysed the heat requirements in a calciner for a carbonation–calcination capture system. It concludes that low purge values minimize the heat requirement at calciner. When fuel has no sulphur and no ashes the minimum heat demand is reached for a given CaO/CO_2 molar ratio of 3.0 and a purge percentage of 4.3%. If a fuel with 16% ash content on dry basis is used, the purge percentage value increases up to 6.1% and the optimal molar ratio reduces to 2.6. When a fuel with 6% sulphur content on dry basis is fed to the calciner, the make-up flow sharply increases and the minimum heat requirements are 25% higher than under the reference case.

A different minimum is found in our calculations for each CaO/CO_2 ratio. These values are located within a narrow range of purge percentages, between 1 and 2%. These minimum costs are slightly over those previously presented for carbonator due to the fact that solid mass flow at calciner (mainly CaO) is lower than at carbonator ($CaCO_3$). Again when the CaO/CO_2 ratio increases, the minimum CO_2 avoided cost is set at lower purge values. The slope of the curve decreases when solid flow within the system gets low; similar conclusions to those settled for the previous case are obtained although minimum cost values for molar ratio of 5 and 4 are closer when solids are purged in the calciner. Optimum scenario is achieved when a molar ratio of 5 and a purge percentage around 1.5% are chosen. These conditions lead to CO_2 avoided costs below €13.2/tCO_2. Results obtained for molar ratio of 4 and purge percentage around 2–2.5% are quite near the already mentioned minimum cost. In the last case, the solid mass flows from carbonator to calciner and from calciner to carbonator are 1008 and 902 kg/s, respectively. Approximately the same amounts of coal, fresh $CaCO_3$ and oxygen need to be feed to the system, 37.0, 23.0 and 75.2 kg/s. Extra net output of 272.6 MW is produced with a COE of €43.0 MW^{-1}.

3.1. Sensitivity analysis

If capture efficiency, η_{capt}, is limited to a maximum of 70% due to hypothetic incomplete gas–solid mixing and/or short resident time, CO_2 avoided cost increases an average of €1.5–2.0/tCO_2 and similar trends to those illustrated in Fig. 5 are observed. The minimum CO_2 avoided cost achieved when CaO/CO_2 molar ratio is 4 and purge percentage from carbonator is 2%, is found below €14.5/tCO_2. The same conclusion may be settled when purging from the calcination reactor, but cost values increase up to €14.8/tCO_2 for CaO/CO_2 ratio equals to 5 and purge percentage of 1% and up to €15.0/tCO_2 for CaO/CO_2 ratio equals to 4 and purge percentage of 2%. In the optimum case, a carbonator CO_2 capture efficiency of 67.1% is achieved. The costs of the new facility are lower than those for the reference case plant because the system has a smaller size. Maximum solid circulation from carbonator to calciner is 929.6 kg/s, and the capture process requires 31.0 kg/s of coal, the same mass flow of fresh $CaCO_3$ 22.5 and 63.2 kg/s of oxygen to calciner. An extra gross power output of 302.4 MW represents a net power output of 228.7 MW. The total investment is M€1180 for the integrated system, with a cost of electricity (COE) of €42.1 MWh^{-1}.

The influence of coal composition has also been analysed. A set of simulations has been carried out with a low-rank high sulphur coal (36% C, 25% H_2O, 24% ashes, 5.5% S, 12.7 MJ/kg) in the original power plant. For oxyfuel combustion has been always supposed a high-rank low-sulphur coal. The main effect is an important solid circulation due to $CaSO_4$ formation in carbonator, solid from carbonator or calciner doubled for a purge of 2% but it is 26% higher for a 10% purge. This result in larger CFB's especially for low purge values, increasing a 35% the TCR for a 2% purge and an 11% for a 10% purge. Nevertheless, heat from the circulating solid increases the steam production and the net power output. There is an equilibrium purge percentage around 3.5% where both effects are balanced. Smaller purge percentages are favourable for low sulphur coal with lower COE (€1 kWh^{-1} for a 2% purge from €43.1 to €44.1 kWh^{-1}), and higher purges are favourable for high sulphur coal causing a reduction in COE around €0.5 kWh^{-1} for a 10% purge. As a consequence capture cost follows the same trend, the lowest capture values are obtained for low purge-low sulphur or high purge-high sulphur combination. With a 2% purge, the capture cost of sulphur coal are €13.2/tCO_2 compared to €12.7/tCO_2 for the reference coal. Nonetheless for a 10% purge the capture cost for high sulphur coal is €13.6/tCO_2 and 14.0 for the reference coal.

4. Conclusions

CO_2 capture systems based on calcium solid sorbent require an intensive solid circulation, the development of oxyfuel technologies and high energy requirements. However these challenges are close to being overcome with the development of CFB oxyfuel technology. The CETC-O laboratory in Ottawa, for example, has demonstrated this concept using a pilot-scale dual fluid bed with calcinations achieved by oxyfuel combustion [22]. The energy requirements allow the integration of the system into a supercritical steam cycle combining a post-combustion capture system and oxyfuel. Thus the CO_2 captured proceeds from both post-combustion and oxyfuel combustion with additional power production which leads to reduced CO_2 capture costs.

All the capture systems based on sorbent technologies mainly depend on sorbent concentration and degradation. Carbonation–calcination systems are influenced by CaO/CO_2 molar ratio and sorbent deactivation ($CaSO_4$ generation and CaO cyclic deactivation). High CaO/CO_2 molar ratios improve the carbonation conversion but increase the cost of the system due to higher solid circulation. High make-up flows also improve the carbonation conversion and hence the CO_2 capture, but increase the heat demand at calciner and the sorbent cost.

Calculations show that minimization of tCO_2 avoided cost is achieved with high CaO/CO_2 molar ratio and low purge percentages. Molar ratios about 5 require a minimum purge of 1% but process economics is very sensitive to purge. If CaO/CO_2 molar ratio is reduced when purge is removed from carbonator, purge has to be increased up to 2–3% to obtain optimum capture cost below €12.8/tCO_2. If purge is designed in calciner, the cost increases around €0.5/tCO_2. All results show that cost remains below €20/tCO_2. Low values of CaO/CO_2 ratio and purge percentages over 5% must be avoided.

Sensitivity analysis shows a small increase of CO_2 capture cost when the carbonation efficiency is reduced, as an example, for a poor solid mixing contact. This increase is around €1.5–2.0/tCO_2. The influence of coal sulphur content on the capture cost is lower, around €0.5/tCO_2 for a 2% purge percentage. However, the capture cost for 10% purge percentage when fueling a high sulphur coal is €0.4/tCO_2 lower than the reference case. In all studied cases the capture cost remains competitive.

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References

[1] B. Metz, O. Davidson, H. de Coninck, M. Loos, L. Meyer (Eds.), Special Report on Carbon Dioxide Capture and Storage Intergovernmental Panel on Climate Change, Cambridge University Press, 2005.

[2] J.C. Abanades, The maximum capture efficiency of CO_2 using carbonation/calcination cycle of $CaO/CaCO_3$, Chem. Eng. J. 90 (2002) 303–306.

[3] J.C. Abanades, E.J. Anthony, J. Wang, J.E. Oakey, Fluidized bed combustion systems integrating CO_2 capture with CaO, Environ. Sci. Technol. 39 (2005) 2861–2866.

[4] T. Shimizu, T. Hirama, H. Hosoda, K. Kitano, M. Inagaki, K. Tejima, A twin fluid-bed reactor for removal of CO_2 from combustion processes, Trans. IChemE 77 (Pt A) (1999) 62–68.

[5] J.C. Abanades, E.J. Anthony, D.Y. Lu, C. Salvador, D. Alvarez, Capture of CO_2 from combustion gases in a fluidized bed of CaO, AIChE J. 50 (2004) 1614–1622.

[6] N. Rodriguez, M. Alonso, G.S. Grasa, J.C. Abanades, Heat requirements in a calciner of $CaCO_3$ integrated in a CO_2 capture system using CaO, Chem. Eng. J. 138 (2008) 148–154.

[7] V. Nikulshina, C. Gebald, A. Steinfeld, CO_2 capture from atmospheric air via consecutive CaO-carbonation and $CaCO_3$-calcination cycles in a fluidized-bed solar reactor, Chem. Eng. J. 146 (2009) 244–248.

[8] D.K. Lee, An apparent kinetic model for the carbonation of calcium oxide by carbon dioxide, Chem. Eng. J. 100 (1–3) (2004) 71–77.

[9] C. Salvador, D. Lu, E.J. Anthony, J.C. Abanades, Enhancement of CaO for CO_2 capture in an FBC environment, Chem. Eng. J. 96 (1–3) (2003) 187–195.

[10] E.H. Baker, The calcium oxide–carbon dioxide system in the pressure range 1–300 atmospheres, J. Chem. Soc. 70 (1962) 464–470.

[11] G.S. Grasa, J.C. Abanades, M. Alonso, B. González, Reactivity of highly cycled particles of CaO in a carbonation/calcination loop, Chem. Eng. J. 137 (2008) 561–567.

[12] V. Manovic, E.J. Anthony, Sequential SO_2/CO_2 capture enhanced by steam reactivation of a CaO-based sorbent, Fuel 87 (2008) 1564–1573.

[13] D. Mess, A.F. Sarofim, J.P. Longwell, Product layer diffusion during the reaction of calcium oxide with carbon dioxide, Energy Fuels 13 (1999) 999–1005.

[14] S.K. Bhatia, D.D. Perlmutter, The effect of product layer on the kinetics of the CO_2–lime reaction, AIChE J. 29 (1983) 79–86.

[15] P. Sun, J.R. Grace, C.J. Lim, E.J. Anthony, Removal of CO_2 by calcium based sorbents in the presence of SO_2, Energy Fuels 21 (2006) 163–170.

[16] P. Sun, J.R. Grace, C.J. Lim, E.J. Anthony, Sequential capture of CO_2 and SO_2 under FBC conditions, Environ. Sci. Technol. 41 (2007) 2943–2949.

[17] P. Sun, J.R. Grace, J.C. Lim, E.J. Anthony, Proceedings of the 18th International Conference on Fluidized Bed Combustion, Toronto, May 2005.

[18] E.S. Rubin, C. Chen, A.B. Rao, Cost and performance of fossil fuel power plants with CO_2 capture and storage, Energy Policy 35 (2007) 4444–4454.

[19] J.C. Abanades, G.S. Grasa, M. Alonso, N. Rodriguez, E.J. Anthony, L.M. Romeo, Cost structure of a postcombustion CO_2 capture system using CaO, Environ. Sci. Technol. 41 (2007) 5523–5527.

[20] L.M. Romeo, J.C. Abanades, J.C. Ballesteros, A. Valero, J.M. Escosa, A. Giménez, C. Cortés, J. Paño, Process optimization in postcombustion CO_2-capture by means of repowering and reversible carbonation/calcination cycle, in: 8th International Congress on Greenhouse Gas Control Technologies GHGT-8, Trondheim, Norway, June 2006.

[21] L.M. Romeo, J.C. Abanades, J.M. Escosa, J. Paño, A. Giménez, A. Sánchez-Biezma, J.C. Ballesteros, Oxyfuel carbonation/calcination cycle for low cost CO_2 capture in existing power plants, Energy Convers. Manage 49 (2008) 2809–2814.

[22] D. Lu, R. Hughes, E.J. Anthony, In situ CO_2 capture using Ca based sorbent looping in dual fluidized beds, in: Pittsburgh Coal Conference, Johannesburg, South Africa, September 2007.