

Heat requirements in a calciner of CaCO₃ integrated in a CO₂ capture system using CaO

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Abstract

Several systems for CO₂ capture using CaO as regenerable sorbent are under development. In addition to a carbonation step, they all need a regeneration step (calcination of CaCO₃) to produce a concentrated stream of CO₂. Different options for calcination may be possible, but they all share common operating windows that appear when the mass and heat balances in the system are solved incorporating equilibrium data, sorbent performance information, and fuel composition (sulphur and ash content). These relatively narrow operating windows are calculated and discussed in this work. Due to sorbent performance limitations, low carbonation levels of the sorbent in the carbonator are expected and the heat demand in the calciner is dominated by the heating of inert solids flowing in the carbonation chemical loop. High make up flows of fresh limestone reduce this effect by increasing the average reactivity of the sorbent, but they also increase the heat demand in the calciner to calcine the fresh feed of limestone. Hence, an optimum level of sorbent activity appears under different operating conditions, processes and fuel characteristic, and these are discussed in this work.

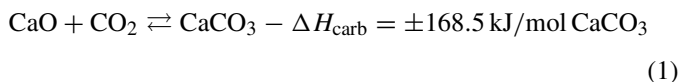
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1. Introduction

Capturing (separating) the CO₂ from large stationary sources (like power plants, cement plants, steel mills, refineries, etc.) and storing it permanently in suitable geological formations, can be a major mitigation option for climate change [1]. It is generally agreed that CO₂ capture and storage can be done by putting together technologies that are already in place today in large industrial applications [1]. However, it is also generally agreed that there is time and scope to explore and develop alternative CO₂ capture systems, better suited for specific power plant boundary conditions. The driving force for these R&D efforts must be to lower the cost and to lower the energy penalties associated with the separation step.

Several of these novel systems are based on the carbonation/calcination loop to separate CO₂ at high temperature using the reversible reaction:



This reaction can be applied in pre-combustion routes, aimed at large scale production of H₂ from coal, natural gas or other carbonaceous materials like biomass (see review [1,2] for further references, and more recent [3,4]). But our main focus in this paper is on a range of postcombustion systems [5] that have shown a large potential for low capture cost [6–9]. Large combustion plants (in particular coal combustion plants) are by far the largest CO₂ sources in the world and they dominate the power generation sector in most countries. They are likely to continue to do so in the next few decades, considering the long life span of these large infrastructures, and the high rate at which these are being built in some developing countries with plenty of coal resources like China. The market potential for new, cost effective CO₂ postcombustion systems is therefore vast.

The schematic process considered in this work is shown in Fig. 1. Flue gases from an exiting power plant (or any other large source) will enter the carbonator, react with CaO to form CaCO₃, and leave the system as flue gas depleted in CO₂ (depending on the capture efficiency in the carbonator). All the

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Nomenclature

C_p	heat capacities ($J/^\circ \text{mol}$), calculated from [23]
E_{carb}	CO_2 capture efficiency in the carbonator
E_{equil}	carbonation efficiency reaching the equilibrium conditions
F_{CO_2}	CO_2 from the combustor to the carbonator (kmol/s)
F_0	fresh make up of sorbent (kmol/s)
F_{Ash}	molar flow rate of ashes between carbonator and calciner (kmol/s)
F_{CaO}	CaO stream between carbonator and calciner (kmol/s)
F_{CaSO_4}	molar flow rate of CaSO_4 between carbonator and calciner (kmol/s)
H_{in}	heat requirement in the calciner (MJ)
H_{comb}	total heat input to the power plant (MJ)
ΔH_{carb}	calcination heat reaction at 900°C (MJ/mol)
ΔH_{LHV}	low heat value for the fuel (MJ/kg)
k	constants proposed in Eq. (3)
N	number of carbonation/calcination cycles
$r_{\text{C/S}}$	carbon to sulphur molar ratio in the fuel
r_N	fraction of sorbent particles that has experienced N calcinations
S_N	fraction of particles that have been cycling in the carbonation–calcination loop more than N times
ΔT_{calc}	temperature gradient between calciner and carbonator (K)
ΔT_{F0}	temperature gradient between calciner and fresh make up stream (K)
w_C	weight fraction of carbon in the fuel
X_{ave}	maximum conversion attainable by the average sorbent particle circulating in the carbonation–calcination loop
X_{carb}	average conversion attained by the sorbent in the carbonator reactor
X_N	carbonation conversion of a particle in the N th carbonation–calcination cycle

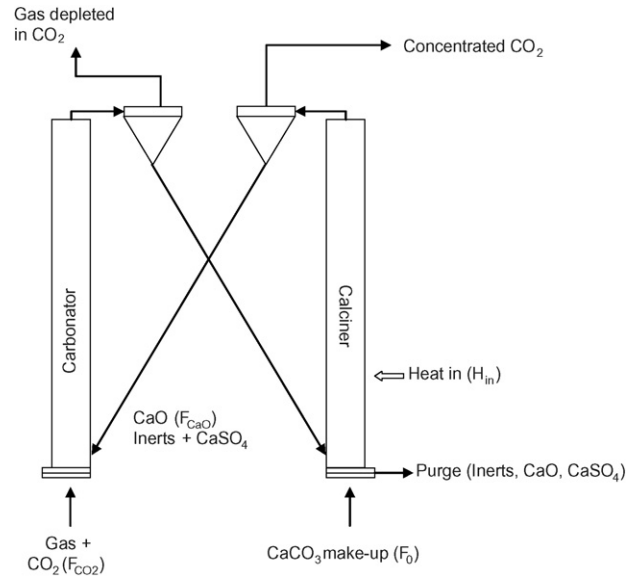


Fig. 1. Scheme of the process for CO_2 capture using the carbonation–calcination loop of CaO .

CO_2 at 1 atm. The rapid development expected by key manufacturers [9,12] for oxy-fired combustion using circulating fluidized bed combustors (CFBCs), should facilitate soon this calcination option. In fact, it could be argued that operation of these oxy-fired CFBC systems should be easier (in terms of temperature control in the bed at high O_2 concentration) when there is an endothermic reaction like calcination of CaCO_3 taking place in the combustor. Therefore, the discussion that follows can be carried out irrespective of the calcination method, but keeping also in mind that the heat requirements in the calciner need to be kept to the minimum irrespective of the calcination method.

The purpose of this work is to analyse how the heat demand in the calciner changes for different operating conditions and design fuels when using the carbonation–calcination loop of

solids including the carbonate carrying the CO_2 are then directed through standpipes to a calciner. Due to the endothermic reaction of calcination and the need to heat up solid streams, a large heat flow has to be supplied to the calciner. Several options could be feasible, but the nearest option to demonstration is to choose a calciner to operate like an oxyfired circulating fluidized bed combustor (which has its own developing path in several large projects in US and Europe). The concept of Fig. 1 was first published by Shimizu et al. [10].

All CO_2 capture system incorporating the carbonation–calcination loop share a common challenge: to supply to a fluidised bed of solids a large amount of heat to drive the calcination reactions in an atmosphere with a high concentration of CO_2 . The equilibrium of CaO/CaCO_3 that is plotted in Fig. 2 for the temperature range of interest for this work [11] imposes a temperature for calcination higher than 900°C for regeneration in

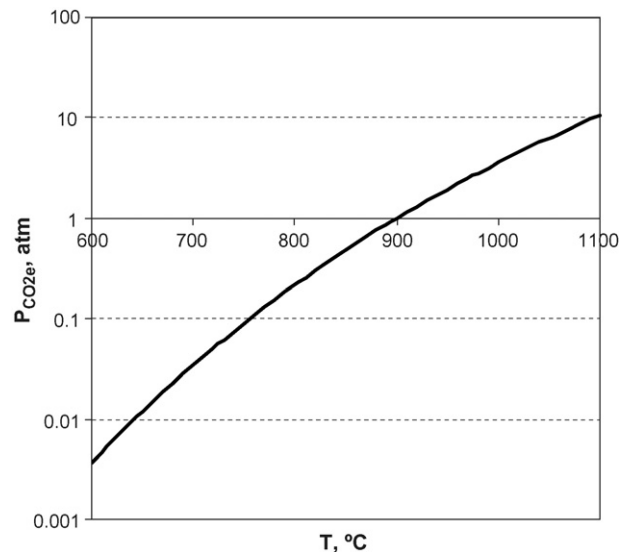


Fig. 2. The equilibrium pressure of CO_2 on CaO .

Fig. 1. Or in other words, what set of operating conditions can be chosen for a given fuel and process scheme to minimize the heat requirements in the calciner. To answer this question we need to solve the mass and heat balances in the system of Fig. 1, incorporating equilibrium and sorbent performance and reactor data as well as fuel composition (sulphur and ash content in the incoming fuels or flue gases).

2. The circulating mass flows of CaO required for effective CO₂ capture

The purpose of a system as depicted in Fig. 1 is to separate CO₂ in concentrated form in the calciner so that this is suitable for geological storage, after purification and compression (not shown in the diagram). Ideally, most of the carbon in the CO₂ stream leaving the calciner, should originate from the carbon contained in the carbonate. Some CO₂ will also originate from the decomposition of the make up flow of limestone fed to system to maintain the activity of the sorbent in the carbonation reactor (see below). CO₂ may also come from the oxy-combustion of the coal fed to the calciner to drive regeneration reactions. Therefore, as indicated in Fig. 1, there is a flow of CO₂ entering the carbonator reactor and reacting with CaO (F_{CaO}) contained in the solid flow coming from the calciner. In the most general case, this stream will be composed of CaO, CaSO₄, ash and any other inert material present in the incoming solid streams to the system (fuels and fresh sorbent make up). The resulting solid stream from the carbonator will contain a certain fraction, X_{carb} , of the total calcium converted to CaCO₃ that will determine the efficiency in the capture of CO₂ from the combustion gases in the carbonator.

$$F_{\text{CaCO}_3} = F_{\text{CO}_2 \text{ captured}} = F_{\text{CaO}} \times X_{\text{carb}} \quad (2)$$

This carbonate will be regenerated back to CO₂ and CaO in the calciner. The heat input, H_{in} , to the calciner is required to drive the endothermic calcination reaction of CaCO₃ and heat up all the solids from the carbonation temperature to the calcination temperature.

In principle, X_{carb} can take any value from zero to the maximum average carbonation conversion achievable by the CaO particles cycling in the system. We call this the maximum average conversion, X_{ave} , because it represents the average conversion of the solid attained when a sufficient large inventory of solids in the carbonator is maintained, to allow sufficiently high residence times of the solids. As reviewed in previous works, the carbonation reaction of CaO can progress in a fast reaction regime at temperatures over 600 °C [13–15] and typical concentrations of CO₂ in flue gases. A solid residence time of a few minutes should therefore be enough to achieve conversions close to X_{ave} . However, it is important to understand the limits to the value of X_{ave} [16] imposed by the poor sorbent performance of CaO as regenerable sorbent submitted to many carbonation–calcination cycles. It has been well documented from early works, including continuous pilot testing in interconnected fluidized beds [17], that natural calcium oxide and dolomites are able to carbonate in the fast reaction regime up to

a maximum level of conversion, X_N that decays with an increasing number of cycles. In a recent paper [18] we have shown that the trend of this decay, up to 500 cycles, follows the equation proposed by Wang and Anthony [19] adding a residual activity:

$$X_N = \frac{1}{1/(1 - X_r) + kN} + X_r \quad (3)$$

This equation is based on a second order sintering mechanism of the sorbent, and it fits well with $k=0.52$ and $X_r=0.075$ most data available for many limestones, and a wide variety of operating conditions (limestone type, particle sizes, carbonation atmosphere and temperature, calcination atmosphere and temperature up to 950 °C). The value of X_r in Eq. (3) would be the maximum carbonation conversion of the sorbent in a continuous system with no make up flow of sorbent (no consumption of fresh limestone), and no deactivation agents of sorbent (like SO₂). Although this is a modest value of conversion, it still translates into a CO₂ capture capacity of 60 mg/g of sorbent, which compares very favourably with most adsorbents proposed to capture CO₂ [20]. However, the solids entering the carbonator of Fig. 1 can be tailored to yield much higher carbonation conversions, by adding a make up flow of fresh limestone (the end of the fast carbonation for the first calcine takes place at values of X_1 around 0.7, 10 times higher than X_r). A mass balance for this CaO recycle system with make up flow of fresh CaO was solved elsewhere [16] and provides an expression for the fraction of solids entering the carbonator that have circulated N times through the loop of Fig. 1:

$$r_N = \frac{F_0/F_{\text{CaO}}}{(1 + F_0/F_{\text{CaO}})^N} \quad (4)$$

So, the fraction of particles that are been in the system at least N cycle is:

$$S_N = 1 - \sum_{N=1}^N r_N = \left(\frac{1}{(F_0/F_{\text{CaO}}) + 1} \right)^N \quad (5)$$

Fig. 3 represents this function together with Eq. (3), for values of F_0/F_{CaO} reasonable for the loop of Fig. 1. Although low values of F_0/F_{CaO} are always desirable in any sorption–desorption system (low consumption of fresh sorbent make up), it has been discussed elsewhere [21] that the very low cost of limestones allows for high F_0/F_{CaO} (in the order of 0.1) without escalating the sorbent cost. As can be seen in Fig. 3, for low values of F_0/F_{CaO} the representative conversion of the sorbent is given by X_r . For high values of F_0/F_{CaO} the largest fraction of sorbent particles in the loop can correspond to those that have been in the system only a few times and can yield much higher conversions.

The average capture capacity of the CaO circulating in the system is given by:

$$X_{\text{ave}} = \sum_{N=1}^{N=\infty} r_N X_N \quad (6)$$

For the case of sorbent deactivation by CaSO₄ formation, it is assumed that all the sulphur present in the fuel reacts quantitatively with the active part of CaO, and therefore all the sulphur

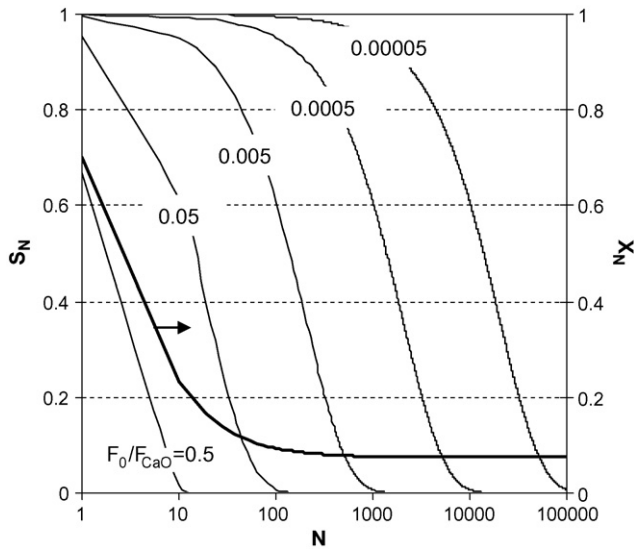


Fig. 3. X_N and S_N , as a function of number of cycles at different ratios of F_0/F_{CaO} .

leaves the system in the solid drain (F_0):

$$X_{ave} = \sum_{N=1}^{N=\infty} r_N X_N - \frac{F_{CO_2}}{F_{Orc/S}} \quad (7)$$

where $r_{C/S}$ is the C/S mol ratio in the fuel. New data [21] indicate that this may be an excessively conservative assumption because part of the CaO not active for the carbonation can actually be active for the sulphation reaction as well. Furthermore, since the $CaSO_4$ formed on the free surfaces of CaO of the sorbent is always in low conversion (the Ca/S ratio entering the system is at least one order of magnitude higher than the used for desulphuration systems, because the C/S ratio is very high even in high sulphur fuels) the SO_2 cannot introduce pore blocking mechanism, that are known to reduce the availability of more CaO in the reaction with SO_2 . In the absence of better quantitative information, the Eq. (7) is adopted in this work, assuming that the fate of all S entering the system will be to irreversibly deactivate only the “CO₂ active” part of CaO (fraction defined by Eq. (4)) forming $CaSO_4$. Fig. 4 represents X_{ave} for a range of conditions of interest. Clearly, the CO₂ capture capacity of the sorbent (X_{ave}) could be kept high in the carbonator despite the decay in sorbent activity, by increasing the fresh feed ratio (F_0/F_{CO_2}). Values of X_{ave} below zero in Fig. 4 correspond to a lack of sufficient fresh limestone to maintain the capture of the sulphur contained in the fuel as $CaSO_4$.

The mass balances for the system of Fig. 1 can now be completed for different fuels and sorbent make up flow ratios, in order to calculate all the solid and gas streams in the system, necessary to achieve a certain CO₂ capture efficiency (Eq. (2)). This has been done for 4 different ideal fuel compositions, characteristic of different sulphur and ash contents and associated flue gas compositions. The calculations have been carried out using a Matlab code that yields identical solutions to those used with commercial process simulation software used in previous works [5], but has the benefit of integrating new sorbent performance models like Eqs. (6) and (7) and allow a fast evaluation

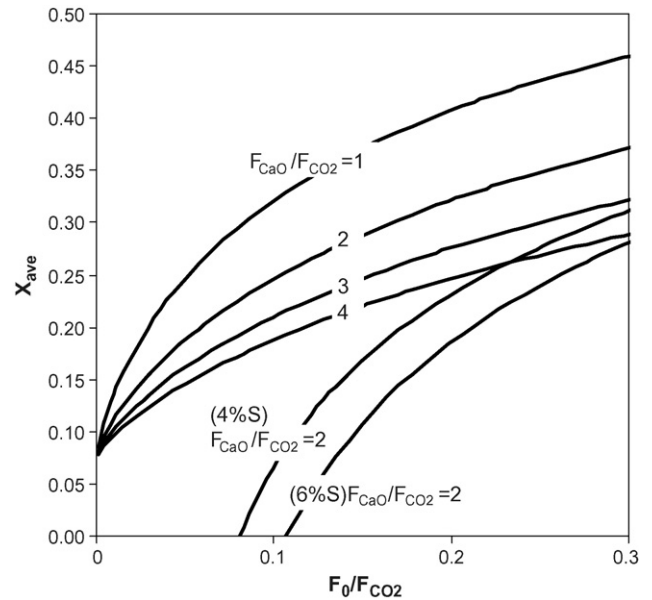


Fig. 4. X_{ave} as a function of ratios F_0/F_{CO_2} and F_{CaO}/F_{CO_2} including the effect of S at low 4% and high 6% fraction.

of the model for different sorbent flow ratios (Figs. 5–8). The ratio F_0/F_{CaO} represents the make up flow of limestone to the system. This defines through the infinite sum of Eq. (7) the maximum capture capacity of the solids circulating between calciner and carbonator, X_{ave} . The conversion of a real carbonator reactor will always have to be lower than X_{ave} . But as mentioned before, if the carbonator was designed with sufficient solid residence time (1–3 min) it should be possible to yield conversions close to the maximum. This was the case in pilot test conducted during the development of the Acceptor Gasification Process [17], although in their case, the high partial pressures of CO₂ would have favoured faster carbonation rates. The actual conversion in the carbonator, X_{carb} , will determine the necessary flow of sorbent between reactors (F_{CaO}) to achieve a given capture efficiency (Eq. (2)) of the reference flow of CO₂ entering the carbonator, F_{CO_2} .

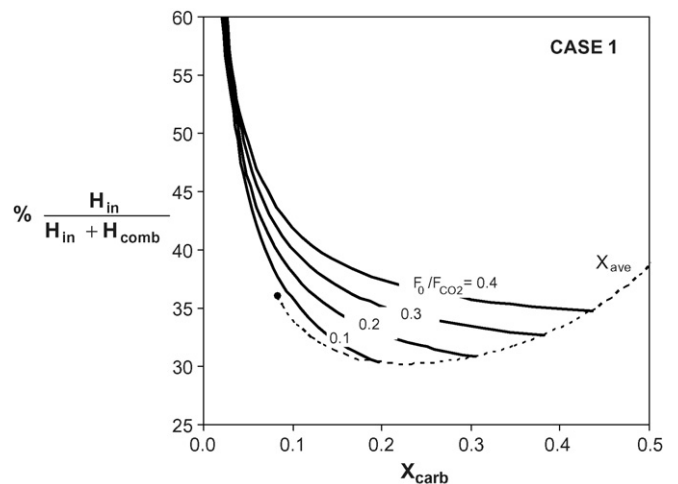


Fig. 5. Heat ratio as a function of CaO conversion at different F_0/F_{CO_2} ratios for reference case 1.

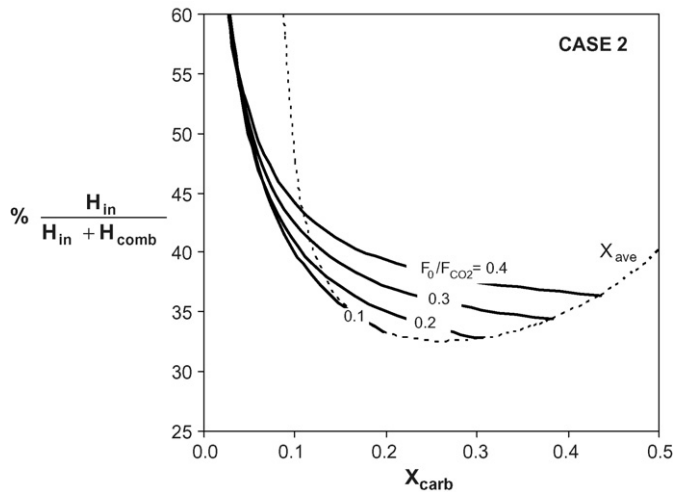


Fig. 6. Heat ratio as a function of CaO conversion at different F_0/F_{CO_2} ratios for reference case 2.

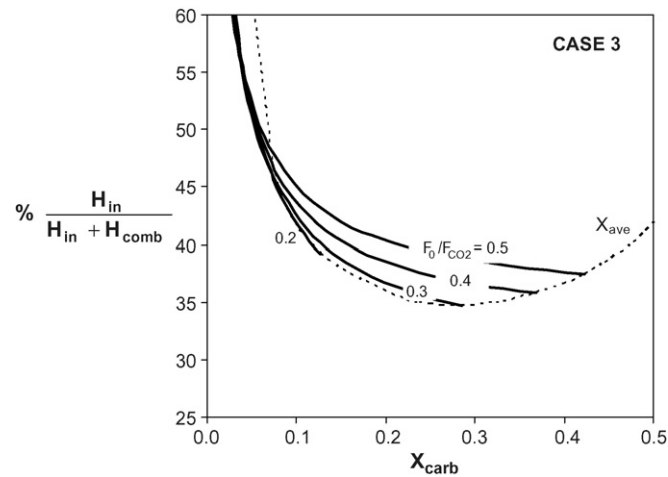


Fig. 7. Heat ratio as a function of CaO conversion at different F_0/F_{CO_2} ratios for reference case 3.

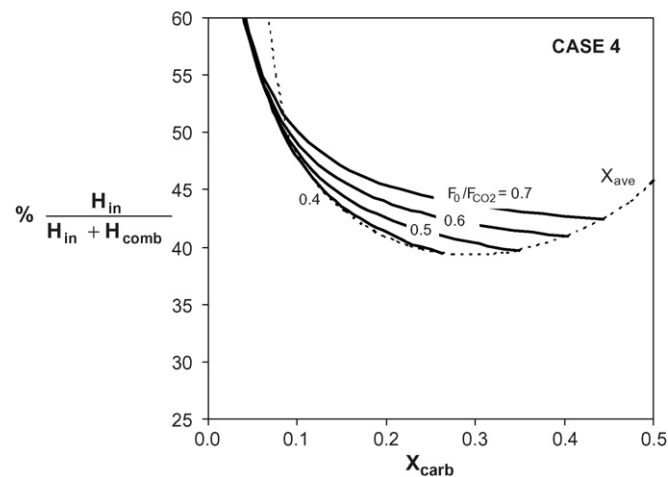


Fig. 8. Heat ratio as a function of CaO conversion at different F_0/F_{CO_2} ratios for reference case 4.

3. Heat requirements for sorbent regeneration

The choice of CaO flow ratios (F_0/F_{CO_2} and F_{CaO}/F_{CO_2}) to achieve the desired capture capacity in the carbonator is not free, because the heat balance in the system will impose further limits on these solid ratios. The calcination of the $CaCO_3$ contained in the solid stream ($F_{CaO} + F_{inert} + F_0$) will involve the supply of heat, H_{in} , to drive the endothermic calcination of the $CaCO_3$ contained in that stream and to heat up to the calcination temperature all the mass streams fed into the calciner (mainly the solid stream from the carbonator). The heat input to the calciner, H_{in} , and the heat input to the combustor (H_{comb}) are defined as:

$$\begin{aligned} \frac{H_{in}}{F_{CO_2}} = & \Delta H_{carb} \left(\frac{F_{CaO}}{F_{CO_2}} X_{carb} + \frac{F_0}{F_{CO_2}} \right) + \Delta T_{cal} \left[C_{pCaO} \frac{F_{CaO}}{F_{CO_2}} \right. \\ & \times (1 - X_{carb}) + C_{pCaCO_3} \frac{F_{CaO}}{F_{CO_2}} X_{carb} + C_{pCaSO_4} \frac{F_{CaSO_4}}{F_{CO_2}} \\ & \left. + C_{pAsh} \frac{F_{Ash}}{F_{CO_2}} \right] + \frac{F_0}{F_{CO_2}} C_{pCaCO_3} \Delta T_{F_0} \end{aligned} \quad (9)$$

$$H_{comb} = \Delta H_{LHV} \frac{12}{w_C} F_{CO_2} \quad (10)$$

where F_{CaSO_4} and F_{Ash} are the molar flow rates of $CaSO_4$ and ash between both reactors. It is assumed for the discussion below that all the individual reactor designs and conditions for the calciner are such that full calcination of the sorbent particles are attained in the calciner.

Figs. 5–8 were all built assuming a carbonation efficiency of 70%. Each point in the figure corresponds to a choice of F_0/F_{CO_2} and X_{carb} . When these two parameters are fixed, the mass balance of Eq. (2) allows the calculation of F_{CaO}/F_{CO_2} . Eq. (7) is used to set the limit imposed by the poor sorbent performance equation (X_{carb} can only vary from zero to X_{ave}) and Eq. (9) can then be used to estimate the heat requirements for the chosen set of X_{carb} and F_0/F_{CO_2} .

Fig. 5 plots the heat ratio defined as the fraction of heat input to the calciner relative to the total heat input to the power plant, $H_{in}/(H_{comb} + H_{in})\%$, as a function of different values of X_{carb} . Fig. 5 has been built for a characteristic example of a flue gas with no ashes and no sulphur (fuel of case 1 in Table 1), and with a temperature gradient between carbonation and calcina-

Table 1
Fuel compositions for the references cases

	Case 1 (%wt)	Case 2 (%wt)	Case 3 (%wt)	Case 4 (%wt)
C	83	65	83	52
H	5	3	5	3
S	0	0	4	6
O	3	8	3	9
N	4	0	0	1
H ₂ O	5	8	5	0
Ash	0	16	0	29
Total	100	100	100	100
LHV (MJ/kg)	34	25	34	21

tion units (ΔT_{cal}) of 300 K (650 °C for carbonator and 950 °C for the calciner). The limit that X_{carb} can reach when all particles in the system reach their maximum conversion, is represented as a dotted line, X_{ave} . As discussed above, this conversion limit is only a function of the F_0/F_{CO_2} ratio when a capture efficiency is imposed. If the X_{ave} is not reached in the system (as will be the case in real reactor systems with incomplete sorbent conversion) the $F_{\text{CaO}}/F_{\text{CO}_2}$ must increase to achieve a certain level of CO_2 capture efficiency from the gas phases. Therefore, as the solid lines indicate, the heat requirements in the calciner increase as X_{carb} diminishes, due to the increasing demand of heat for heating up a the unconverted solid stream from the carbonator.

There is a characteristic point in Fig. 5 (at $X_{\text{carb}} = 0.075$) that has been marked with a solid dot and that corresponds to a situation with no make up flow of limestone ($F_0/F_{\text{CO}_2} = 0$). This would be an ideal system, where the residual activity of the sorbent (CO_2 capture capacity for an infinite number of cycles) would be used (with a $F_{\text{CaO}}/F_{\text{CO}_2} = 9.3$ in this example) to capture the CO_2 in the carbonator (capture efficiency of 70% in this example). This ideal case is only possible if there is no sulphur in the flue gas and no ash accumulation in the carbonation–calcination cycle. The heat requirements are 36.9% of total heat input to the plant for this ideal case. The dotted line of Fig. 5 represents the series of minimum heat requirements for a given make up flow of fresh sorbent to the system. For each F_0/F_{CO_2} , this corresponds to the case where X_{carb} reaches its maximum value allowed by Eq. (6). Fig. 5 shows that this dotted line also has a minimum, where the heat requirements to the calciner is reduced to 30.2% (this correspond to $X_{\text{carb}} = X_{\text{ave}} = 0.23$ for a $F_{\text{CaO}}/F_{\text{CO}_2} = 3.0$ and a $F_0/F_{\text{CO}_2} = 0.13$ in this example). These molar flows correspond to 0.90 kg of fresh limestone/kg of coal fed to the power plant to generate the flue gas entering the carbonator. This minimum appears because the opposite effect that an increase in the make up flow of fresh limestone, F_0/F_{CO_2} , has on the two main components in the definition of H_{in} (Eq. (9)). Low values of F_0/F_{CO_2} lead to low values of X_{ave} , and this means that more heat is required to heat up to the calcination temperature the inert CaO ($1 - X_{\text{ave}}$). An increase of F_0/F_{CO_2} will tend to improve the capture capacity (higher X_{ave}) of the solids flowing between carbonator and calciner. With higher X_{ave} , less solids will be required to circulate between reactors, and the heat requirements for heating solid streams will be reduced. However, the necessary heat to calcine the fresh make up flow, F_0 , will increase, giving rise to the optimum value of F_0/F_{CO_2} that minimizes the overall heat requirement in the calciner.

The quantification of these optimum values of solid flow ratios to minimize the heat requirements in the calciner is important for the design of these systems, because in order to minimize limestone consumption, the economic optimum is likely to be a function of this minimum.

In the discussion above we have not defined the source of the heat input to the calciner. As indicated in the introduction, the most plausible solution at present is to burn a certain amount of coal with O_2 to produce a highly concentrated stream of CO_2 from this calciner [10]. The value of H_{in} will increase slightly in these conditions depending on the level of the preheating of

the additional solid and gas streams (coal, make up, O_2 , CO_2 recycle) entering the calciner.

Fig. 6 presents similar simulation when introducing a fuel containing ash (but negligible sulphur content) into the mass and heat balances. In practice, this can be the case when the carbonator system is treating flue gases before de-dusting equipment. The solid lines of Fig. 6 follow similar qualitative trends as in Fig. 5, with the heat demand increasing rapidly as X_{carb} diminishes for a fixed value of make up flow ratio F_0/F_{CO_2} . The dotted line of Fig. 6 represents again the minimum heat requirements for each make up flow ratio F_0/F_{CO_2} , that shows a minimum for this particular case at 32.5%, with $F_0/F_{\text{CO}_2} = 0.16$ and $F_{\text{CaO}}/F_{\text{CO}_2} = 2.63$. The presence of inert ashes in the carbonation–calcination loop will increase as the make up flow ratio (and associated purge rate) diminishes. Therefore, the dark point that marked in Fig. 5 the heat requirements when operating the system with no make up flow has now moved up to $H_{\text{in}}/(H_{\text{in}} + H_{\text{comb}}) = 1$ when $X_{\text{carb}} = X_{\text{ave}} = X_{\text{r}}$ (which appears when there is no purge rate of solids). The need to purge ashes from the carbonation–calcination loop may determine the choice of F_0/F_{CO_2} . For the particular boundary conditions of Fig. 6 it would be attractive to choose F_0/F_{CO_2} around 0.16 (0.87 kg limestone/kg coal) to moderate the heat requirements in the calciner and purge the ashes introduced by the fuel in the carbonation–calcination loop.

Fig. 7 presents the solution to the mass and heat balances in a system burning a fuel with no ash but high sulphur content (for example, pet coke). Since all sulphur contained in the fuel is assumed to react with the active part of CaO for carbonation, it is necessary to operate with higher F_0/F_{CO_2} ratios. For the particular fuel of case 3, there is a F_0/F_{CO_2} ratio 0.086) just to capture the sulphur contained in the fuel as CaSO_4 . In every other aspect, the figure is qualitatively similar to the case of Fig. 6. A higher minimum heat requirement appears around 34.7%, for a solids conversion of 0.27 and a F_0/F_{CO_2} ratio of 0.29 (2 kg fresh limestone per kg fuel). There may be some conditions where the sulfation reaction (exothermic) could take place also in the calciner (for example, when oxyfiring sulfur containing coal in the calciner). In these cases, Eq. (9) should add this term and the heat requirements in the calciner would be reduced slightly.

Fig. 8 presents the final example with the most challenging fuel in Table 1: a coal with high ash and high sulphur content. This could be the case for highly integrated carbonation–calcination loops (“in situ” CO_2 capture as in reference [5,22]) when carbonation and CO_2 generation by combustion or gasification are taking place in the same reactor. The conditions of pressure and temperature will change for these cases, but the heat and mass balances will result in solutions as represented in Fig. 8. Large F_0/F_{CO_2} ratios are unavoidable both to purge the ashes and to compensate for the deactivation of active CaO as CaSO_4 . The figure is qualitatively similar to the ones above but the minimum heat requirement is now gone up to 39.3% at F_0/F_{CO_2} ratio of 0.43 (1.86 kg of limestone per kg of fuel). The make up is slightly lower than in case 3 because the lower carbon content of the fuel. With cases 3 and 4 the integration of the capture system with a cement plant would be essential, in order to give a use to the large purge of solids, and

take credit of the energy spent to calcine the fresh make up flow of limestone [5].

4. Conclusions

Emerging CO₂ capture systems using CaO as regenerable sorbent of CO₂ require large flows of heat to be supplied to the calciner in order to regenerate the carbonated sorbent by calcination. Although this heat supply can be effectively recovered in the system because all mass streams are at high temperature, it is always interesting to minimize the heat demand in the calciner. The simultaneous solution of heat and mass balances in a general carbonation–calcination cycles, incorporating sorbent performance data, allow the calculation of the heat requirement in the calciner for different fuels and boundary conditions. For flue gases with no ash and no sulphur, aiming at a 70% CO₂ capture, heat requirement around 37% appears when no make up flow of fresh sorbent is required because the carbonate loop relies on the residual activity (7–8%) of the CaO towards carbonation at very high cycle numbers. This heat requirement decreases down to 30% when increasing the F_0/F_{CO_2} because the fresh limestone addition improves rapidly the average activity of the sorbent up to $X_{carb} = 23\%$. From this point, further increases in make up flow of limestone translate into increasing heat requirements, because the heat demand for the calcination of the fresh make up becomes dominant in the heat balance around the calciner. The effect of high ash content in the fuel produce an increase of solid amount circulating in the loop, and this tend to increase the heat requirements. The effect of high sulphur content implies an increase of F_0/F_{CO_2} to compensate for the sulphation of the active part of the CaO. For the case of high ash and sulphur fuel, a larger make up flow of sorbent is needed and a synergy with a cement plant may be necessary.

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