Chemical Engineering Journal 156 (2010) 388–394

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Average activity of CaO particles in a calcium looping system

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ARTICLE INFO

Article history:
Received 7 July 2009
Received in revised form 16 October 2009
Accepted 27 October 2009

Keywords:
CO_2 capture
Carbonation
Deactivation

ABSTRACT

Calcium looping cycles for capturing CO_2 from large emission sources will most likely use interconnected circulating fluidized bed reactors. The mass balances that govern the mixed solids in the main reactors of these systems, combined with a description of sorbent reaction and decay in activity, are used in this work to define the average activity of the material as a function of the sorbent recycling and make up flow ratios. The new formulation of the mass balances takes into account the fact that particles during carbonation and/or calcination achieve partial conversion in the respective reactors. In these conditions, average activity is shown to be a function of not only sorbent properties and make-up flow ratios, but also the internal solid circulation rates between the reactors. Explicit equations are obtained for the average activity of the circulating materials. These equations are used to discuss the effect of the key operating variables on CO_2 capture efficiency. The equations proposed here for the $CaCO_3$/CaO system may also be valid for other chemical reactor systems that use interconnected circulating fluidized beds.

1. Introduction

In order to mitigate the effects of climate change over the next few decades it will be necessary to find a way to balance the use of cheap and widely available fossil fuels, coal in particular, with the ambitious goal of drastically reducing global emissions of CO_2 before 2050 [1]. When the mitigation options take into account the need to ensure the minimum cost of this mitigation, CO_2 capture and storage (CCS) emerges as one of the main options for combating climate change [2]. The devices necessary to deploy CCS on a large scale already exist in the oil, natural gas and chemical industries, and only minor additional investment is required for them to be applied at an even larger scale in the power generation sector. CO_2 capture is known to be the most costly and energy consuming step in the CCS chain. Therefore the goal of many ongoing projects is to develop more energy and cost effective capture methods. One growing area of investigation is that of chemical looping processes. These operate at high temperatures and can theoretically capture CO_2 with minimum energy penalties. Anthony [3] has recently reviewed the development of these processes. From this review it can be seen that they have already entered experimental validation in small pilot plants. The use of the carbonation reaction of CaO with CO_2 and the subsequent calcination of $CaCO_3$ into CaO and CO_2 is one of these promising chemical looping concepts [3]. A schematic of the carbonation–calcination loop is represented in Fig. 1 to illustrating the key gas and sorbent mass streams.

In postcombustion applications, a flue gas containing diluted CO_2 (F_{CO_2} in mole of CO_2/s) is brought in contact with CaO particles to form $CaCO_3$ in the carbonator reactor up to a certain level of conversion. The CaO particles are continuously coming into the carbonator from the calciner in the solids stream, F_R. A make-up flow of limestone (F_0) is introduced into the calciner (or at any other point in the system) and this is balanced in stationary state by an identical flow of CaO (mixed with ashes and other solids if present) leaving the system. The resulting carbonation reaction takes place at temperatures of around 650 °C. Over 900 °C the reverse calcination reaction takes place in the calciner, as a result of which the CaO is regenerated and a concentrated CO_2 stream is obtained.

The material (CaO particles) cycling in the carbonation–calcination loop is known to become deactivated (loss of CO_2 capture capacity) with the number of carbonation and calcination cycles [4–9]. After each cycle, the fraction of active CaO in a particle is usually defined as the carbonation conversion, X_N, which is reached at the end of the rapid carbonation stage. A general equation for this deactivation has been proven to be valid for many limestones up to 500 cycles [8,10]:

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

where k is the deactivation constant (this has a value of 0.52 for many limestones and under many conditions), X_r is the residual conversion of CaO after an infinite number of cycles ($X_r = 0.075$) and N is the number of full carbonation and calcination cycles. Recent works have proposed simple measures to reduce the tendency of

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doi:10.1016/j.cej.2009.10.055

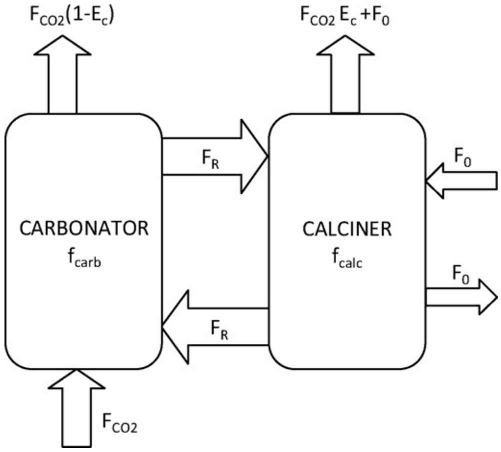


Fig. 1. Schematic of a calcium looping system to capture CO_2 and main gas and solid streams.

deactivation of natural sorbents expressed by Eq. (1) (whereby the effective deactivation constant is reduced and/or the value of the residual activity is increased). Examples of such measures are reactivation methods [11], hydration [12] or treatment of the limestone with doping agents [13]. However for the purpose of our analysis, we have assumed that the decay in conversion is only dependent on the number of cycles as described by Eq. (1).

In a continuous system involving interconnected circulating fluidized beds such as that in Fig. 1, the particles in the fluidized bed reactors are ideally mixed with respect to solid residence time distributions. There is therefore a wide range of particles, with different cycle numbers, constantly present in the system. A mass balance of the carbonate loop of Fig. 1 was carried out in an earlier work [14] to estimate the fraction of particles that have cycled the system N times, r_N, as a function of the circulation rates, F_R, and make-up flow ratio, F_0:

$$r_N = \frac{F_0 F_R^{N-1}}{(F_0 + F_R)^N} \tag{2}$$

The average activity, X_{ave}, or maximum carbonation conversion of a sample of solids from the system, was calculated assuming complete calcination of the sorbent and the total completion of the fast carbonation stage (up to the level given by Eq. (1)) in the reactors of Fig. 1. N would then represents both the number of times that a particle cycles between each reactor and the number of total carbonation–calcination cycles it experiences when the average activity of the solids in the system is defined as:

$$X_{ave} = \sum_{N=1}^{N=\infty} r_N X_N \tag{3}$$

This equation generates explicit equations for X_{ave} (depending on the choice of deactivation curve for X_N), and have been used for reactor designs and systems analysis in previous works (see [15–19]). The equations for X_{ave} are valid as long as the operating conditions and reactor designs allow the maximum conversion of solids during carbonation and calcination. This is most likely to occur in the precombustion applications of the carbonation–calcination loop, because the high temperature and high partial pressures of CO_2 guarantee a very fast carbonation reaction, which was demonstrated experimentally by Curran et al. [9] when developing the CO_2 acceptor process. However, recent indications from modelling and experimental results [17,20–22] suggest that the total carbonation conversion of solids may not be feasible with the typical residence times of particles in a circulating fluidized bed carbonator. This is because the application of calcium looping cycles to large flow rates of characteristic flue gases in postcombustion CO_2 capture systems would require very compact reactor designs (short gas–solid contact times). In these conditions, the carbonator reactor would have to operate at low partial pressures of CO_2 and which would not allow the particles to undergo their maximum conversion. Furthermore, for the system to operate at a reasonable capture efficiency, a certain amount of active material must be present in the carbonator reactor in stationary state [17,20,21,23], which means that it is necessary a certain amount of CaO with capacity to react with CO_2. This requisite implies that partial carbonation of the solids is necessary for the carbonator reactor to be able to operate as an absorber of CO_2.

On the other hand, the need to keep calcination temperatures down in the calciner, in order to avoid materials and ash related problems, means that calcination temperatures should exceed the equilibrium calcination temperature of $CaCO_3$ as little as possible. Therefore, although the conditions for complete carbonation (up to the limit given by Eq. (1)) and complete calcination can be expected given the high rates of carbonation and calcination reactions, these conditions are in fact likely to be somewhat different from what one would expect for an optimum reactor design. In other words, the search for carbonator reactors of minimum size and with small bed inventories that are able to operate at minimum calcination temperatures will inevitably lead to conditions in which carbonation and calcination cannot be completed. The average activity of the sorbent material flowing into the carbonator will be different from that predicted for these conditions of partial solid conversions. And yet an accurate estimation of this average activity is essential for the design of the carbonator reactor. Thus, the objective of this work is to find a general and simple function that expresses the average activity of the sorbent in the carbonate loop of Fig. 1 when only partial carbonation and calcination conversions take place in the reactors.

2. Mass balances with incomplete particle conversion

As mentioned above, Eq. (1) represents the capture capacity of a sorbent after N complete carbonation and calcination cycles and Eq. (2) is the equation used to estimate the fraction of particles that have cycled N times between the carbonator and calciner. However, if the carbonation and calcination reactions are not completed, the two "N" mentioned in the previous sentences are no longer the same. For the purpose of this work, however, we retain the meaning of N as being the number of times that a particle has cycled between the carbonator and calciner. As recently discussed elsewhere [24], since Eq. (1) establishes a link between the total carbonation conversion, and the number of complete carbonation/calcination cycles, we can define a cycle number from the maximum conversion attainable by the sorbent, X_{ave}, which represents the 'reaction age' of the particles, or the cycle number associated to such particles, irrespective of their previous history of partial or complete carbonation/calcination cycles:

$$N_{age} = \frac{1}{k}\left(\frac{1}{X_{ave} - X_r} - \frac{1}{1 - X_r}\right) \tag{4}$$

Furthermore, it is possible to define in the system of interconnected reactors illustrated in Fig. 1 two characteristic conversions of the solids that leave the carbonator (X_{carb}) and the calciner (X_{calc}), and the characteristic changes in carbonation conversion of the solids entering and leaving each reactor. Fig. 2 shows the notation employed for these conversions. Since full conversions are not achieved in the carbonator or in the calciner, it is possible to define the extent or fraction of calcination or carbonation in each reactor,

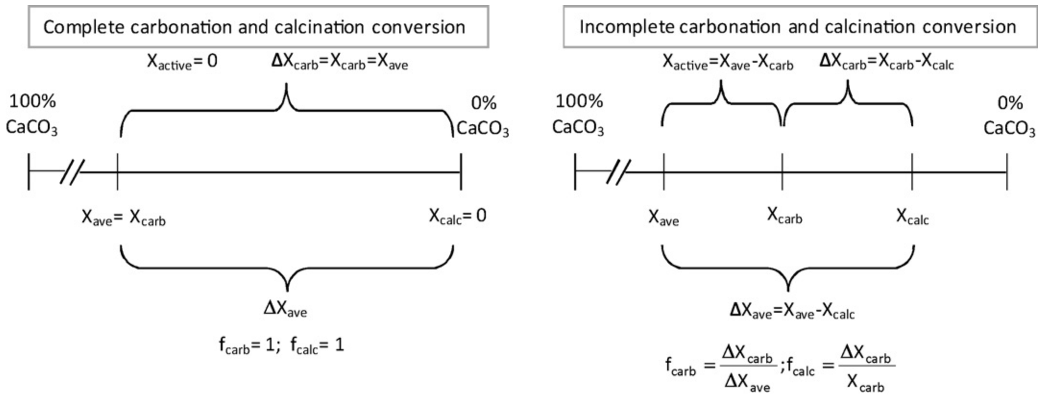


Fig. 2. Definition of the main carbonation conversions involved in the mass balances.

which is as follows:

$$f_{\text{carb}} = \frac{X_{\text{carb}} - X_{\text{calc}}}{X_{\text{ave}} - X_{\text{calc}}} \tag{5}$$

$$f_{\text{calc}} = \frac{X_{\text{carb}} - X_{\text{calc}}}{X_{\text{carb}}} \tag{6}$$

It should be emphasized here that X_{ave} in Eq. (5) is still the average of the maximum carbonation conversion of the family of all particles of the CaO fractions arriving at the carbonator (Eq. (3)). In the carbonator reactor, there will be a certain amount of active solids that have not yet been carbonated and that are responsible for the absorption of CO_2 from the gas phase [17,20,21,23] defined here as X_{active} (see Fig. 2). It is also important to note that the fractions of carbonation and calcination defined above are assumed to apply to all the particles in the system, irrespective of their individual activity or capture capacity. In perfectly mixed reactors, this will not be the case because the large residence time distribution of particles in the bed makes it possible for fully converted particles (long individual residence times) to coexist with particles of low conversion (short residence times). However, it is possible to assume an average conversion that applies to all the particles looping in the system and with this assumption subsequent analysis is greatly simplified. Furthermore, it is also assumed that individual fractions of CaO change their actual age (by Eq. (4)) in discrete mode, by completing a new calcination cycle after their carbonation. In other words, we assume here that partial conversion does not affect the mechanism of decay that leads to Eq. (1) and that a given volume of CaO changes its activity after each calcination cycle.

Following the schematic representations of Figs. 1 and 2 and the previous set of assumptions, the target in this section is to obtain an explicit expression for the average activity, X_{ave} (or maximum carbonation conversion) of the solids entering the carbonator reactor as a function of the solid circulation flows (F_R and F_0) and assumed fractional carbonation and calcination conversions, f_{calc} and f_{carb}.

According to our previous analysis, a certain mass of CaO (particles or fraction of CaO in these particles) has a discrete value of activity that is associated to a specific maximum conversion capability ($X_{N_{\text{age}}}$). A certain fraction of CaO, $r_{N_{\text{age}}}$, that has experienced N_{age} full carbonations and calcinations in the loop, enters the carbonator in the solid stream (F_R). If total carbonation has occurred after complete calcination, $X_{N_{\text{age}}} = X_N$ (Eq. (1)) and $r_{N_{\text{age}}} = r_N$ (Eq. (2)). When the carbonation and/or calcination are not completed, the fraction of CaO, $r_{N_{\text{age}}}$, together with activity $X_{N_{\text{age}}}$, can be calculated from a succession of mass balances by incorporating the fraction of calcination and the fraction of carbonation (f_{calc} and f_{carb}). The first mass balance applies to r_0, which represents the mole fraction of CaO circulating through the loop that has not experienced any calcination (i.e. still in the same form of fresh $CaCO_3$ as when it comes from the make-up flow). The total flow of solids leaving, or entering, the calciner is the sum of F_0 and F_R. There will be an uncalcined flow of fresh limestone from the make-up flow leaving the calciner, $F_0(1-f_{\text{calc}})$, and an uncalcined flow of fresh limestone arriving from the carbonator and leaving the calciner, $F_R r_0(1-f_{\text{calc}})$. Therefore, the fraction of calcium in the system that has never been calcined is:

$$r_0 = \frac{F_0(1-f_{\text{calc}}) + F_R r_0 (1-f_{\text{calc}})}{F_0 + F_R} \tag{7}$$

Or in explicit form:

$$r_0 = \frac{F_0(1-f_{\text{calc}})}{F_0 + F_R f_{\text{calc}}} \tag{8}$$

Note that the absorption capacity of this fraction of CaO is zero ($X_{N_{\text{age}}}$ or X_N is equal to zero when N_{age} or N is zero because not even the first calcination has yet taken place). In contrast, the next fraction of CaO, r_1 represents the mole fraction of CaO or $CaCO_3$ that has experienced just one calcination, i.e., the fraction r_1 is made up of CaO and $CaCO_3$ with an equivalent cycle number $N_{\text{age}} = 1$. r_1 is obtained from a mass balance around the calciner. The mass balance is made up of four terms (all with a CO_2 capture capability or capacity equal to X_1 in Eq. (1)): flow of calcium oxide leaving the calciner resulting from the calcination for the first time of the fresh limestone fed into the calciner ($F_0 f_{\text{calc}}$), flow of calcium oxide cycling in the loop (and therefore arriving from the carbonator) that has never been calcined and is calcined now for the first time ($F_R r_0 f_{\text{calc}}$), flow of calcium oxide cycling in the loop that belongs to cycle number 1 but has never been carbonated in the carbonator reactor, and for that reason they still keep on the same capture capacity of cycle number 1 ($F_R r_1(1-f_{\text{carb}})$) and flow of calcium carbonate cycling in the loop that has been calcined once, it has also been carbonated once, but it is not calcined again when it leaves the calciner ($F_R r_1 f_{\text{carb}}(1-f_{\text{calc}})$). Thus, r_1 is expressed by:

$$r_1 = \frac{F_0 f_{\text{calc}} + F_R(r_0 f_{\text{calc}} + r_1(1-f_{\text{carb}}) + r_1 f_{\text{carb}}(1-f_{\text{calc}}))}{F_0 + F_R} \tag{9}$$

In a similar mass balance, we define r_2 as the mole fraction of CaO with a carbonation conversion that corresponds to cycle number 2 (X_2 in Eq. (1)). The mass fraction of CaO in the system that belongs to r_2 is made up of: flow of calcium that changes from cycle number 1 to number 2 after being calcined and carbonated for the second time ($F_R r_1 f_{\text{carb}} f_{\text{calc}}$), flow of calcium that has been calcined twice but it has been carbonated only once, thus its capture capacity is kept on the cycle number 2 ($F_R r_2(1-f_{\text{carb}})$) and flow of calcium that has been calcined and carbonated twice, thus it is already part of the fraction of calcium of cycle number 2, but in their third chance to be calcined in the calciner, they are not calcined ($F_R r_2 f_{carb}(1-f_{calc})$).

$$r_2 = F_R \frac{r_1 f_{carb} f_{calc} + r_2(1-f_{carb}) + r_2 f_{carb}(1-f_{calc})}{F_0 + F_R} \tag{10}$$

It can be seen that the general term for the fraction of CaO in the cycle N_{age} is given by Eq. (11).

$$r_{N_{age}} = \frac{(r_0 + (F_0/F_R)) f_{carb}^{N_{age}-1} f_{calc}^{N_{age}}}{((F_0/F_R) + f_{carb} f_{calc})^{N_{age}}} \tag{11}$$

Note here that Eq. (1), which represents how any fraction of calcium (originally as $CaCO_3$ in the fresh limestone) decreases the capacity to react with CO_2 with the number of cycles, is still valid for this system. It is assumed that when the carbonation and calcination reactions are not completed, particles will end up with a variety of Ca fractions ($r_0, r_1, r_2, \ldots, r_{N_{age}}$) within the particle, but the evolution of the activity in each of these fractions of CaO will still be governed by Eq. (1). Eq. (2) is also valid for this system, but the physical meaning of r_N is different from the physical meaning of $r_{N_{age}}$ above. In the first case, r_N is the fraction of CaO that has cycled N times between carbonator and calciner. In Eq. (11) $r_{N_{age}}$ is the fraction of CaO and $CaCO_3$ that has been fully calcined N_{age} times after $N_{age}-1$ complete carbonations. Complete carbonation and complete calcination can take place in many partial steps, so that N is always larger than N_{age} except when $f_{calc} = f_{carb} = 1$ (Eq. (11) becomes Eq. (2) when this happens). However, when it is a question of defining the average activity of the material, we can still define this as an infinite sum of small contributions from each fraction of material with an activity $X_{N_{age}}$. Therefore, we can rewrite Eq. (3) as:

$$X_{ave} = \sum_{N_{age}=1}^{N_{age}=\infty} r_{N_{age}} X_{N_{age}} \tag{12}$$

We have not been able to find an explicit expression for this sum when using Eq. (1) for $X_{N_{age}}$ and Eq. (11) for $r_{N_{age}}$. But the solution is straightforward when deactivation of CaO (Eq. (1)) is approached as a geometric progression [14]. However, to retain the quality of the fit provided by Eq. (1) for the real deactivation curves, it is convenient to put this equation into the form recently proposed by Li et al. [17]:

$$X_{N_{age}} = a_1 f_1^{N_{age}+1} + a_2 f_2^{N_{age}+1} + b \tag{13}$$

where the fitting constants, $a_1 = 0.1045$, $f_1 = 0.9822$, $a_2 = 0.7786$, $f_2 = 0.7905$ and $b = 0.07709$, fit the data of Eq. (1) with a regression square coefficient higher than 0.99, which means that $X_{N_{age}}$ in Eq. (13), represents virtually the same deactivation curve as the one expressed by Eq. (1). The advantage of approximating Eq. (13) to Eq. (1) is that when substituting Eq. (13) into Eq. (12) it is then possible to calculate the limit of the infinite sum of the geometric series and calculate the maximum average conversion by means of the following equation:

$$X_{ave} = (F_0 + F_R r_0) f_{calc} \left[\frac{a_1 f_1^2}{F_0 + F_R f_{carb} f_{calc}(1-f_1)} + \frac{a_2 f_2^2}{F_0 + F_R f_{carb} f_{calc}(1-f_2)} + \frac{b}{F_0} \right] \tag{14}$$

This is a key purpose designed equation for calcium looping systems because it links the key sorbent performance parameters with the main solid circulation flows and reactor performance indicators (f_{carb} and f_{calc}) providing a way to estimate the average activity of the material circulating between the reactors.

It is now possible to analyze the impact of partial carbonation and calcination on systems where the same CO_2 capture parameters are maintained constant. For this purpose, we define here the molar flow of the CO_2 captured as:

$$F_c = E_c F_{CO_2} \tag{15}$$

The mass balance in Fig. 1 also defines CO_2 capture efficiency as:

$$E_c = \frac{F_R \Delta X_{carb}}{F_{CO_2}} \tag{16}$$

Carbonation conversion of solids in the carbonator reactor ($\Delta X_{carb} = X_{carb} - X_{calc}$) is maximum when the carbonation and calcination reactions are completed, since X_{carb} will be equal to X_{ave} and X_{calc} will be equal to zero. When the reactions are not completed, the carbonation conversion can be expressed as function of the partial carbonation and calcination as follows:

$$\Delta X_{carb} = f_{carb} f_{calc} X_{ave} \tag{17}$$

Thus, the sorbent molar flow circulating between the reactors (F_R) can be expressed as a function of the CO_2 molar flow captured (F_C), the partial carbonation and calcination fractions (f_{carb}, f_{calc}), and the maximum average conversion attained in the carbonator (X_{ave}):

$$F_R = \frac{F_c}{f_{carb} f_{calc} X_{ave}} \tag{18}$$

Hence, in the next sections we will discuss the effect of f_{carb} and f_{calc} on the average capture capacity of the material circulating in the system for different ratios of characteristic flows of material in the capture system.

3. Effect of solid circulation rates on average activity

In order to discuss the effect of the main solid circulation rates on the average activity of the sorbent we shall begin with a case where complete calcination is achieved in the calciner ($f_{calc} = 1$), where Eq. (14) becomes:

$$X_{ave} = \frac{a_1 f_1^2 F_0}{F_0 + F_R f_{carb}(1-f_1)} + \frac{a_2 f_2^2 F_0}{F_0 + F_R f_{carb}(1-f_2)} + b \tag{19}$$

Eq. (19) is represented in Fig. 3 to show how the maximum average conversion (continuous lines) increases for the same molar ratio F_0/F_R, at different values of f_{carb} and when capture efficiency is set to 0.9. The carbonation conversion (X_{carb}) reached in the reactor is indicated by dotted lines for each carbonation fraction (Fig. 3). As can be seen from this figure, the effect of incomplete carbonation in the system for any value of F_0 and F_R is an increment of X_{ave} for decreasing numbers of the partial carbonation fraction.

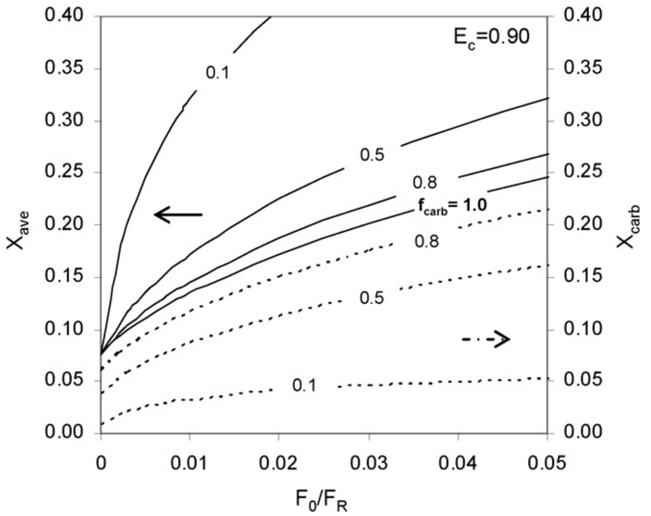


Fig. 3. Maximum average conversion and carbonation conversion attained as a function of the molar flow relation F_0/F_R for different partial carbonation conversions ($f_{calc} = 1$, $E_c = 0.9$).

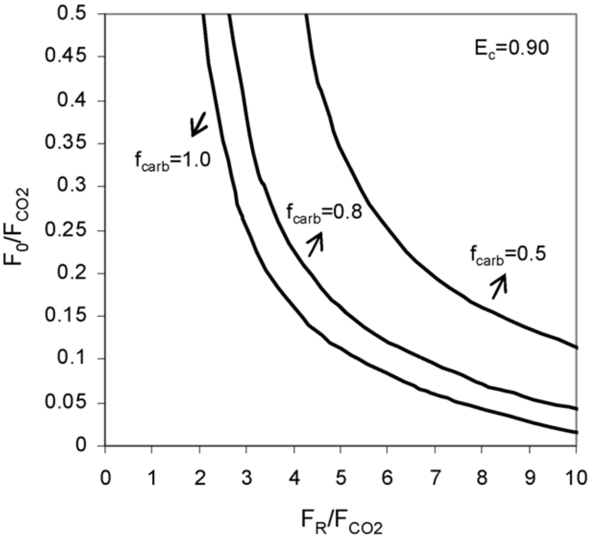


Fig. 4. Relationship between the make-up and recycled flow ratios in order to achieve a target capture efficiency of CO_2 for different fractions of carbonation reaction.

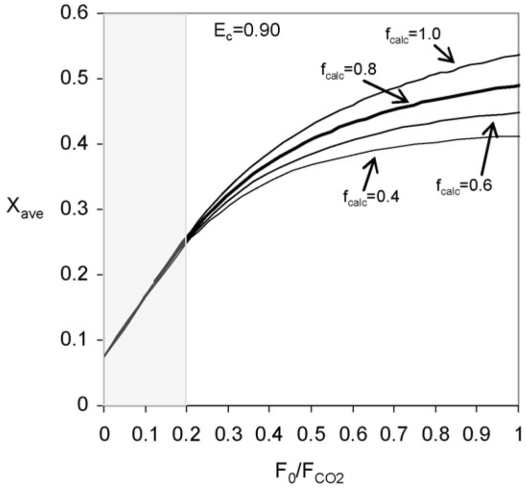
This seems a radical improvement with respect to full carbonation conditions because the active phase (X_{active}) in the carbonator reactor increases as X_{ave} increases and X_{carb} decreases. However, this apparently positive result is misleading because the improvements are at the expense of the increase in the solid circulation rates F_R necessary for the same flow of carbonate to be transported between reactors when the carbonation conversions decrease (see Eq. (16)). Furthermore, since Fig. 3 represents the results as a function of F_0/F_R, the necessary increase in F_R to compensate for lower X_{carb} under partial carbonation conditions also entails an increment of F_0 to maintain the F_0/F_R ratios constant, thereby causing a further increase in the average activity of the materials as a result of the increase in the make-up flow of limestone.

As pointed out above, once the CO_2 capture parameters (E_c and F_{CO_2}) are fixed, the flow ratios F_0/F_{CO_2} and F_R/F_{CO_2} are connected by the mass balance (Eqs. (14) and (16)). In order to clarify this point, Fig. 4 represents the relationship between the make-up and recycle flow ratios for different values of f_{carb}. This is a critical point in design choice for achieving the desired capture efficiency: high values of make-up flow (which will increase the operational cost of the capture system of Fig. 1 if no use is found for the solids purged from the deactivated CaO) or high values of internal solid circulation rates (which will increase heating requirements in the calciner among other problems). In principle, any one of the points on the solid lines indicates a set of conditions under which it would be possible to capture 90% of the CO_2 fed into the carbonator. Points on the left hand side of the curve represent systems with circulating solids of high average activity because of the large value of the F_0/F_{CO_2} make up flow. These systems require the lowest solid circulation values between reactors, F_R/F_{CO_2}. The partial carbonation of the solids requires a higher value of F_R/F_{CO_2} and therefore all solid lines move to the right. As discussed in previous paragraphs, this means that the average activity of the material increases since partial carbonation is achieved at the expense of an increase in internal solid circulation. Thus, both increasing the make-up flow and increasing the partial carbonation have the same effect of increasing the average activity of the material. In summary one might argue from Fig. 3 that partial carbonation introduces a net benefit into the design at no apparent extra cost. However, Fig. 4 highlights the opposite effect of partial carbonation on the other key parameter in the reactor design: the solid circulation rate increases proportionally as the value of partial carbonation decreases provided that the make-up flow is kept constant. Therefore, the apparent benefit of partial carbonation (increasing the average activity of the circulating material) has to be weighed against its negative effect on the increase in solid circulation.

Another way to analyze in more detail the effect of partial carbonation on maximum average conversion once capture efficiency is set to a certain value, is by substituting F_R (Eq. (18)) into $r_{N_{age}}$ (Eq. (11)) when f_{calc} = 1. The following expression for $r_{N_{age}}$ is thus obtained:

$$r_{N_{age}} = \frac{(F_0/F_C)X_{ave}}{((F_0/F_C)X_{ave}+1)^{N_{age}}} \quad (20)$$

It can be seen from this implicit equation that the maximum average conversion of any type of CaO in the system is actually independent of the fraction of carbonation (f_{carb}) as long as full calcination takes place after carbonation. Then, under full calcination conditions, the average activity of the solids in the loop is only determined by the flow of fresh make-up limestone to the system. The flow of solids' cycling affects the solids' conversion in the carbonator. For a given flow of CO_2 capture, higher solid circulation flows lead to partial carbonation conversion and in addition, this will improve the average activity of the circulating solids according to Eq. (20).



f_{carb}	f_{calc}	r_0	X_{ave}
1	1	0	$r_N \cdot X_N$
1	0	1	$r_0 \cdot 0=0$
0	1	0	$(1-r_0)^*X_1$

Fig. 5. Maximum average conversion attainable in the carbonator as a function of the F_0/F_{CO_2} ratio for different fractions of calcination (f_{carb} = 1.0).

The question now arises as to what happens when calcination is not completed in the calciner ($f_{calc} < 1$). The first thing to note is that r_0 (Eq. (7)), or the fraction of calcium from the make-up flow that has never been calcined, is greater than zero. These particles therefore do not have the capacity to capture CO_2. Their activity is considered to be zero despite their potential to yield particles with the highest possible capture capacity after the first calcination. By substituting F_R (Eq. (18)) into $r_{N_{age}}$ (Eq. (11)) when f_{calc} and f_{carb} are not equal to one, the following general equation is obtained for the fraction of CaO in the N_{age} cycle:

$$r_{N_{age}} = \frac{(((F_0/F_C)(1-f_{calc})X_{ave})/((F_0/F_C)f_{carb}X_{ave}+1)) + (F_0/F_c)f_{calc}X_{ave}}{((F_0/F_c)X_{ave}+1)^{N_{age}}} \quad (21)$$

Unlike Eq. (20), Eq. (21) shows that, in this case, the maximum average conversion of particles in the system is indeed affected by the fraction of partial calcination (f_{calc}) and the fraction of partial carbonation (f_{carb}) when complete calcination is not achieved. Thus, the activity of the solids in the loop (represented by Eq. (12)) is determined not only by the flow of fresh make-up limestone (as in the case of complete calcination) but also by f_{carb} and f_{calc}.

Fig. 5 shows the maximum average carbonation conversion as a function of the F_0/F_{CO_2} ratio when f_{calc} takes different values. For the sake of simplicity f_{carb} is considered to be equal to one in the figure. Once the capture efficiency is set to a certain value, the figure shows that the effect of the partial calcination and/or carbonation becomes significant when the make-up flow of fresh limestone, F_0, is high. The decrease in X_{ave} with lower values of f_{calc}, is more pronounced when F_0/F_{CO_2} has values higher than 0.2. However, it must be emphasized that the looping system for capturing CO_2 is unlikely to work with such a large flow of fresh limestone ($F_0/F_{CO_2} = 0.2$ would entail make-up flows of limestone of about 1 kg limestone/kg of coal). The grey area in the figure shows a more feasible operating window.

The decrease in X_{ave} as f_{calc} decreases is due to the increase in the fraction of calcium that has never been calcined, r_0. When calcination is incomplete and F_0 increases, there will be an increasing amount of fresh $CaCO_3$ entering the carbonator reactor. r_0 is always lower than f_{calc} because, as Eq. (7) shows, r_0 depends on both the make-up flow and the recycled flow ratios. For instance, the fraction of r_0 is 19% of the total amount of solids in the system when f_{calc} is 0.4 and the ratio F_0/F_{CO_2} is 1. This means that only 19% of the particles have not yet been calcined despite the low value of f_{calc}. This is because the circulation system offers the particles more than one opportunity to calcine even when the calciner is operating at low values of f_{calc}.

It can be concluded from the previous analysis that, once the capture efficiency is fixed, and given a feasible operating window of make-up flows ($F_0/F_{CO_2} < 0.2$) partial calcination does not significantly affect the average maximum conversion provided that there is no limit to the flow of CaO being recycled. Of course, this is not a realistic supposition because there are well established limits to the solid circulation flows between reactors, as discussed with reference to Fig. 4. It will always be necessary to take into account the F_R/F_{CO_2} ratio.

Fig. 6 shows the capture efficiency attained in the carbonator reactor as a function of the F_0/F_{CO_2} ratio and for two different values of recycled flow. As shown in the figure, the increase in the activity of the solids inside the reactor due to partial carbonation (e.g. $f_{carb} = 0.8$ and $f_{calc} = 1$), does not benefit the capture efficiency unlike complete carbonation and calcination ($f_{carb} = f_{cal} = 1$) when the recycled flow of CaO is fixed. As discussed in previous paragraphs, higher values of carbonation and calcination (f_{carb} and f_{calc} close to 1) lead to higher capture efficiencies for the same solid circulation rates. However, in these conditions, the active fraction of calcium ($X_{ave} - X_{carb}$) will be low and a very high amount of solids will be needed for the bed inventory to achieve a good capture efficiency. There is then a clear tradeoff between these two effects, and the equations proposed in this work could be very useful for optimizing the design of the system.

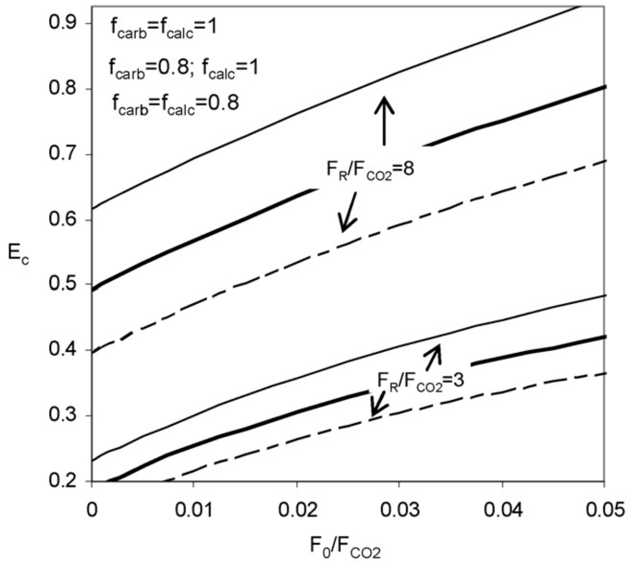


Fig. 6. CO_2 capture efficiency in the loop using different flow ratios.

4. Conclusions

CaO looping system can be designed to capture CO_2 from flue gases by means of cycling carbonation and calcination reactions. Large solid flows between reactors will lead to limited residence times of particles in each of their pass through the carbonator or calciner reactors. Complete carbonation and calcination conversions may not take place and particles will have to cycle between carbonation and calcination reactors a higher number of times in order to transport the same amount of CO_2. For a fixed value of capture efficiency the effect of incomplete carbonation and calcination will translate an increase in the average capture capacity of the circulating material. However, the active phase in the circulating solids will increase at the expense of an increase in solid circulation rates. Therefore, the relative benefit achieved from incomplete particle conversions will be the lower solid inventory required in the carbonator reactor thanks to the increase in the active fraction of calcium. However this advantage needs to be offset against the limitations on the reactor design imposed by the increment of the solid circulation rates, that tend to increase the heat requirements in the calciner.

Notation

E_c	CO_2 capture efficiency in the carbonator reactor
f_{calc}	fraction of calcination of all the particles in the system
f_{carb}	fraction of carbonation of all the particles in the system
F_0	molar flow of fresh make-up limestone fed into the system (mol/s)
F_C	molar flow of CO_2 captured (mol/s)
F_{CO_2}	molar flow of CO_2 that enters the carbonator reactor (mol/s)
F_R	molar flow of recycled solids inside the loop (mol/s)
k	general deactivation constant for limestones
N	number of calcination and full carbonation cycles
N_{age}	equivalent number of full carbonation and calcination cycles for a sorbent to reach its current maximum conversion potential (measured as $X_{N_{age}}$)

r_0	fraction of calcium in the system as $CaCO_3$ that has never been calcined
r_N	fraction of calcium that have cycled between carbonator and calciner N times
$r_{N_{age}}$	fraction of calcium that have been fully calcined N_{age} times after at least $N_{age}-1$ complete carbonations
X	molar conversion of CaO to $CaCO_3$
X_{active}	CaO reacting in the fast reaction regime in the carbonator
X_{ave}	maximum average carbonation conversion attainable by the solids in the system
X_{calc}	conversion to $CaCO_3$ of solids leaving the calciner
X_{carb}	conversion to $CaCO_3$ of solids leaving the carbonator
X_N	maximum carbonation conversion achieved after N calcination and full carbonation cycles
$X_{N_{age}}$	maximum carbonation conversion achieved in a full carbonation cycle irrespective of the history of the sorbent in terms of previous calcination–carbonation cycles
X_r	general residual conversion of limestones after an infinite number of cycles
ΔX_{carb}	carbonation conversion of solids in the carbonator reactor
ΔX_{ave}	maximum possible carbonation conversion possible in the carbonator reactor

Acknowledgements

N. Rodríguez acknowledges a fellowship grant awarded by FICYT (Asturias-Spain). Funding supplied by Endesa and Hunosa is also acknowledged.

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