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Chemical Engineering Journal 90 (2002) 303–306

Chemical Engineering Journal
www.elsevier.com/locate/cej

Short communication

The maximum capture efficiency of CO_2 using a carbonation/calcination cycle of $CaO/CaCO_3$

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Received 21 March 2002; accepted 31 May 2002

Abstract

The use of natural calcium carbonates as regenerable CO_2 sorbents in industrial processes is limited by the rapid decay of the carbonation conversion with the number of cycles carbonation/calcination. However, new processes are emerging to capture CO_2 using these cycles, that can take advantage of the intrinsic benefits of high temperature separations in energy systems. This work presents an analysis of a general carbonation/calcination cycle to capture CO_2, incorporating a fresh feed of sorbent to compensate for the decay in activity during sorbent re-cycling. A general design equation for the maximum CO_2 capture efficiency is obtained by incorporating to the cycle mass balances a simple but realistic equation to estimate the decay in sorbent activity with the number of cycles.

Keywords: CO_2 capture; CO_2 separation; Carbonation; Calcination

1. Discussion

Carbon dioxide from fossil fuel burning is the major contributor to the greenhouse effect from human activities. Within the many options and actions for mitigation of greenhouse gas emissions, CO_2 capture and sequestration is emerging as a viable options to achieve the very deep cuts in emissions that might be needed in the medium term [1]. In the longer term, one can envisage that a power plant combining CO_2 capture and sequestration with biomass firing would be transformed in a net absorber of CO_2 from the atmosphere. It is generally accepted [2] that the cost associated with the separation of CO_2 from flue gases introduces the largest economic penalty to this mitigation option. This justifies a range of emerging approaches to separate CO_2 with more cost-effective processes.

This paper concerns the use of the carbonation reaction of CaO and the reversible calcination of $CaCO_3$ as a suitable separation process of CO_2 (Fig. 1). In the carbonator, a certain gas flow (F_{gas}) containing diluted CO_2 (F_{CO_2} in kmol/s) is put in contact with a sorbent containing CaO at temperatures typically over 600 °C and the carbonation reaction takes place to form $CaCO_3$. The reverse calcination reaction takes place in the calciner at higher temperatures, to regenerate the sorbent. The background for such a CO_2 separation goes back to 1867, when DuMotay and Marechal first proposed using lime to aid the gasification of carbon by steam [3]. A century later, the CO_2 acceptor gasification process reached a demonstration phase [4] using the carbonation/calcination of CaO from limestones or dolomites to separate CO_2 from coal gasification gases. In these early processes, the release of CO_2 during calcination was not an issue and the heat for calcination was supplied by combustion of part of the fuel with air. The need to obtain a purified stream of CO_2 from the calciner is relatively new. Shimizu et al. [5] proposed a cycle for combustion applications involving the regeneration of the sorbent in a calciner using CO_2/O_2 mixtures to burn part of the fuel. Silaban et al. [6] studied the reversibility of this reaction in dolomites and limestones as the base of a high temperature separation of CO_2 to produce hydrogen [6,7]. A similar process is being integrated in a new concept for a power plant [8] to produce H_2 from carbonaceous materials. There is a parallel process being developed in Japan [9] that also includes a carbonation/calcination cycle to produce H_2 from gasification. Finally, the reversible carbonation/calcination reaction of Fig. 1 has also been proposed as the base of energy storage systems [10,11] and as a chemical heat pump [11,12].

A key issue for any of the previous processes is how fast and in what extent reactions take place in the reactors of Fig. 1, and how these rate parameters vary in the subsequent cycles carbonation/calcination. The first studies on the reversibility of the carbonation/calcination reaction

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PII: S1385-8947(02)00126-2

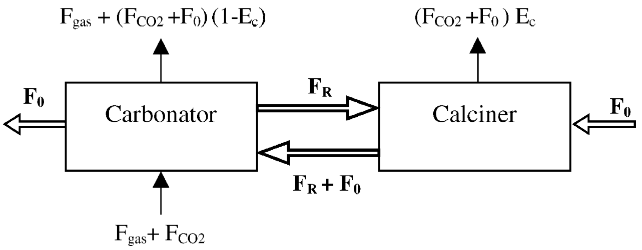

Fig. 1. Outline of a lime carbonation/calcination cycle to separate CO_2 from flue gases.

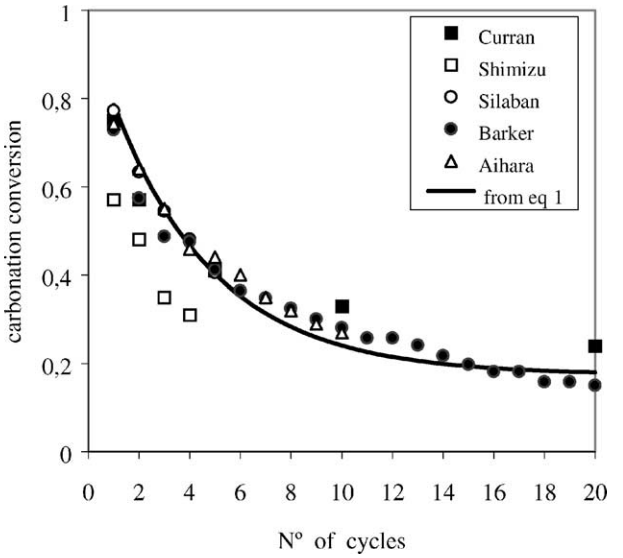

Fig. 2. The evolution with the number of carbonation/calcination cycles of the maximum carbonation capacity of CaO from different authors (see reaction conditions in Table 1).

showed that the recarbonation is far from reversible in practice [4,10,13]. After a very rapid, chemically controlled, initial reaction period a much slower second stage is followed, controlled by diffusion in the $CaCO_3$ layers [4,10,13,14]. The transition between the fast and slow reaction periods takes place quite suddenly at a given level of conversion [13,14]. From a practical point of view, i.e. to allow a compact design of the carbonator of Fig. 1, only the fast reaction period is of interest. This work is only concerned with the "maximum" carbonation conversion, $x_{c,}$ that marks the end of the fast carbonation rate period and that decays rapidly when using limestones. Although, the decay of this carbonation conversion can be smoother in the case of dolomites [4,6], this benefit is offset by the need to circulate inert MgO in the cycle of Fig. 1, which can make more energy demanding the regeneration of the sorbent in the calciner. Also, a range of synthetic sorbents incorporating CaO have been proposed for some of the processes outlined earlier [11,15]. This is at the expense of increasing the cost of the sorbent and the addition of an inert material to the cycle of Fig. 1.

Fig. 2 presents several series of experimental data published on the decay of maximum lime carbonation conversion with the number of cycles. Table 1 provides an overview of the very different range of conditions employed in the experimental systems used in the different series of data collected in Fig. 2. Considering these differences in reaction times and conditions, it is striking the similarity of results presented in Fig. 2. Only the four data from Shimizu et al. [5] fall slightly apart of the common trend. These authors carried out the calcination at relatively close conditions to the equilibrium (atmosphere of pure CO_2 and 950 °C) which are known to enhance the internal sintering associated with the decay in sorbent activity. It is beyond the scope of this short communication to analyse in detail the mechanism behind the experimental evidence shown in Fig. 2. For the purpose of the analysis carried out later, it seems reasonable to assume that the decay in conversion is only dependent on the number of cycles and not on the reaction conditions and reaction times used in the original experiments. In fact, all the data of Fig. 2 can be fitted to the following equation:

$$x_{c,N} = f^{N+1} + b \tag{1}$$

The constants $f = 0.782$ and $b = 0.174$ produce a correlation coefficient of 0.982, which is of remarkable quality (solid line in Fig. 2) considering the simplicity of the equation and the dispersion in reaction conditions in Table 1. Mess et al. [14] observed that the end of the fast reaction period in non-porous particles of CaO was marked by the formation of a product layer with a thickness in the order of 0.1 μm. Barker [10] showed that the carbonation reaction can be fully reversible ($b = 1$) for particles sizes below this thickness. Therefore, the residual carbonation conversion, b, of Eq. (1) can be justified with the formation of a product layer of $CaCO_3$ inside the large voids still present in highly sintered particles. This is a subject for a more detail investigation that is beyond the scope of the present work.

Table 1
Outline of reaction conditions during the series of experiments of Fig. 2

Authors [reference]	Carbonation		Calcination		Particle size (mm)	N cycles
	T (K)	P_{CO_2} (atm)	T (K)	P_{CO_2} (atm)		
Curran [4]	1089	1.3	1333	4	>1	70
Shimizu [5]	873	0.05	1223	1	0.5	4
Silaban [6]	1023	0.15	1023	0	0.038	5
Barker [10]	1139	1.0	1139	0	0.02	25
Aihara [11]	1023	0.2	1023	0	10 (pellet)	10

Reconsidering now the process diagram of Fig. 1, it is assumed here that for most of the practical applications of the carbonation/calcination cycle, compact reactor designs and reactor conditions can be found to achieve the full calcination of the sorbent and the full completion of the fast carbonation stage (up to the level given by Eq. (1)). Examples of processes where this is the case have been referred earlier [4,5,8,9] for both combustion and gasification applications. The decay in conversion of the sorbent and the need to moderate the heat supply to the calciner impose some limits to the CO_2 capture efficiency. Let us assume that the objective in the design is to estimate this limit in CO_2 capture efficiency for a given set of values of F_0 and F_R. A mass balance on Fig. 1 defines the CO_2 capture efficiency as:

$$E_{CO_2} = \frac{(F_R + F_0)\bar{x}_c}{F_{CO_2} + F_0} \qquad (2)$$

where F_{CO_2} is the flow of CO_2 entering the system in the flue gases (in mol/s) and F_R and F_0 are solid flows (in mol/s) of CaO. The estimation of the average conversion of particles in the recycle, $\bar{x}_c$, requires the knowledge of the population of particles in F_R in terms of the number of times that they have experienced the carbonation/calcination cycle (N in Eq. (1)). Let us assume that solids are well mixed in both the carbonator and the calciner, as it is the case in the reviewed examples operating with fluidised beds [4,5]. The mass fraction of particles, r_N, entering the carbonator in the solid stream $F_0 + F_R$ (mol CaO/s), that have circulated N times through the loop of Fig. 1 is calculated from a succession of mass balances:

$$\begin{aligned} r_1 &= \frac{F_0}{F_0 + F_R} \\ r_2 &= \frac{r_1 F_R}{F_0 + F_R} \\ &\vdots \\ r_N &= \frac{F_0 {F_R}^{N-1}}{(F_0 + F_R)^N} \end{aligned} \qquad (3)$$

Since the conversion of each of these population of particles is only determined by the number of cycles (Eq. (1)). The average conversion in the carbonator is given by:

$$\bar{x}_c = \sum_{k=1}^{k=\infty} r_k x_{c,k} \qquad (4)$$

To calculate the previous infinite sum, we take into account that the limit of an infinite sum of the geometrical progression is:

$$\sum_{k=0}^{k=\infty} s^k = \lim \frac{1 - s^{k+1}}{1 - s} = \frac{1}{1 - s}, \quad |s| < 1 \qquad (5)$$

Therefore, incorporating Eqs. (1) and (3) into Eq. (4):

$$\bar{x}_c = \frac{fF_0}{F_0 + F_R(1 - f)} + b \qquad (6)$$

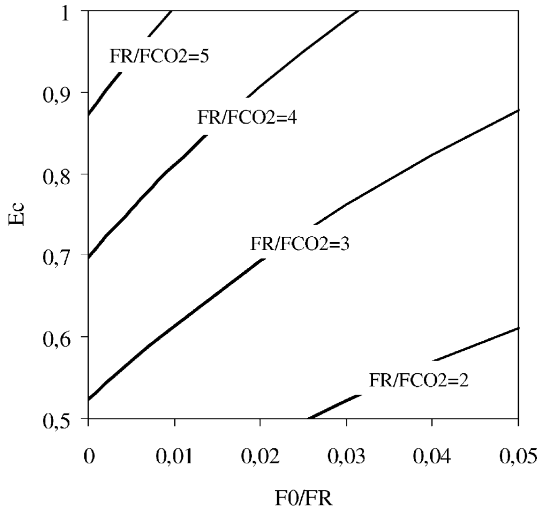

Fig. 3. Maximum efficiency in the capture of CO_2 with a lime carbonation calcination cycle using different recirculation ratios as in Eq. (7).

or in terms of the maximum CO_2 capture efficiency (Eq. (2)) attainable with this sorbent as a function of the flow ratios F_0/F_R and F_{CO_2}/F_R:

$$E_{CO_2} = \frac{1 + (F_0/F_R)}{(F_0/F_R) + (F_{CO_2}/F_R)} \left[\frac{f(F_0/F_R)}{(F_0/F_R) + 1 - f} + b \right] \qquad (7)$$

Fig. 3 represents this equation in a range of values of F_R/F_{CO_2} and F_0/F_R with practical interest. The first ratio is limited by heat balance considerations in the regeneration of the sorbent. High values of F_R/F_{CO_2} can lead to unrealistic amounts of energy to be transferred to the regenerator in order to heat up the solids coming from the carbonator (where temperatures are typically 150–300 K lower than in the calciner). On the other hand, it is also clear that low values of F_0/F_R are desirable to keep the needs of fresh sorbent under reasonable values. It might be illustrative to think on the large quantities of limestone used today in some power stations for sulphur control, and consider that C/S mol ratios higher than 50 are common even in fuels with moderately high sulphur content. The low values of F_0/F_R can not be achieved by increasing indefinitely the recycle flow F_R, because the regeneration of the sorbent in the calciner requires heat to be transferred to this reactor, as mentioned earlier. Finally, this compromise between moderate values of F_R and low values of F_0, keeping low the ratio between them, can be struck with sorbents more insensitive to the decay in conversion with the number of cycles. However, this is a subject for future investigations. Eq. (7) can be used as a simple tool to optimise these key operating and design parameters in CO_2 separation processes using the lime carbonation calcination cycle. It also emphasises that high capture efficiencies of CO_2 can be obtained with natural limestones working as regenerable sorbents in the emerging processes being proposed to capture CO_2 from combustion and gasification gases.

Acknowledgements

This work is part of a project partially funded by the European Coal and Steel Community (7220-ED-125).

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