Chemical Engineering Journal 163 (2010) 324–330

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Effect of sorbent hydration on the average activity of CaO in a Ca-looping system

B. Arias [a,*], G.S. Grasa [b], J.C. Abanades [a]

[a] Instituto Nacional del Carbón, CSIC, C/Francisco Pintado Fe, No. 26, 33011, Oviedo, Spain
[b] Instituto de Carboquímica, CSIC, C/Miguel Luesma Castán, No. 4, 50015 Zaragoza, Spain

ARTICLE INFO

Article history:
Received 8 June 2010
Received in revised form 2 August 2010
Accepted 3 August 2010

Keywords:
CO_2 capture
Ca-looping
Sorbent regeneration
Hydration

ABSTRACT

It is well known that the solid sorbents used in calcium looping CO_2 capture systems experience a reduction in carrying capacity with the number of cycles. Several sorbent reactivation schemes have been proposed as means of overcoming this deactivation process. This work analyzes the integration of a reactivation process in a Ca-looping cycle by means of a hydration reactor. The mass balances involved in this three-reactor systems must then be solved in order to evaluate the effect of the different variables on the average activity of the sorbent. The positive impact of reactivation by hydration (i.e. average increase in activity of the sorbent arriving at the carbonator) is discussed in conjunction with the negative impacts on the overall operation of the system (e.g. steam consumption, etc.) and on the large reactivation reactors. Two different scenarios employing different degrees of hydration have been evaluated. The results obtained show that steam is used more efficiently when only a small fraction of the circulating solids is hydrated to a high degree. Moreover, the performance of the sorbent reactivation step is better when low make up flows of limestone are used.

1. Introduction

Calcium looping is rapidly developing into a viable technology for CO_2 capture from combustion flue gases and hydrogen production systems [1–4]. In all the calcium looping systems for CO_2 capture, the carbonation reaction of CaO with CO_2 is followed by the reverse calcination reaction of $CaCO_3$ in order to regenerate the CaO in a pure atmosphere of CO_2 or CO_2/H_2O. Low price natural limestones and dolomites are generally considered to be the best CaO precursors for large scale CO_2 capture in power plants. However, the capture capacity of these CaO sorbents is known to decay rapidly with the number of carbonation calcination cycles [5,6]. In spite of the decay in the maximum CO_2 capture capacity of CaO derived from natural rocks, it has been demonstrated that a sufficient make up flow of fresh limestone can compensate for this decay at a reasonable cost [7]. Especially when the large purge of solids abandoning the system is used as a feedstock in the cement industry [8]. However, situations may arise where this synergy between calcium looping and cement manufacture will not be feasible. In these cases, minimization of the sorbent make up flow will be an important requirement for process design. One solution [9] would be to take advantage of the residual activity of the CaO sorbents (7–10 percentage points of Ca conversion), which remains stable for many hundreds of cycles and is able to sustain the calcium looping processes at the expense of the large solids circulation flows between the reactors. The other option would be to find methods to improve the sorbents and/or sorbent reactivation techniques.

The search for improved sorbents and/or sorbent reactivation strategies continues in the scientific literature (see Section 4 in the recent review of Blamey et al. [3]). There are clear benefits for the overall performance of the system when more active materials (greater carrying capacity of CO_2 and/or higher reaction rates) are employed. The use of materials with higher CO_2 carrying capacities reduces the solids circulation rates and hence the heat requirements of the calciner [10] and solids make up flows. Higher reactivities also help to reduce the solids inventory in the carbonator reactor, which is necessary in order to achieve a CO_2 capture efficiency of over 90% [11,12]. There are however certain limits to such improvements, as demonstrated by Lisbona et al. [13], in their assessment of the integration of sorbent reactivation methods to a power plant equipped with a CO_2 capture system. Clearly, the cost and/or the energy requirements in the manufacture or reactivation of the sorbent material used in the capture loop need to be carefully assessed for each sorbent and reactivation technique.

One of the most promising low cost methods for enhancing sorbent performance in Calcium looping systems is the partial hydration of the deactivated material [14–17]. The idea of reactivating CaO particles for Calcium looping processes by means of hydration was proposed during the development of the Acceptor Gasification Process during the 1970s [18].

---

[*] Corresponding author. Tel.: +34 985 119057; fax: +34 985 297662.
E-mail addresses: borja@incar.csic.es (B. Arias), gga@incar.csic.es (G.S. Grasa), abanades@incar.csic.es (J.C. Abanades).

1385-8947/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2010.08.009

Nomenclature

E_C	CO_2 capture efficiency in the carbonator reactor
F_{CO_2}	molar flow of CO_2 that enters the carbonator reactor
F_H	molar flow of solids that enters the hydrator reactor
F_{H_2O}	molar flow of steam to the hydrator
F_0	molar flow of make up limestone
F_R	molar flow of solids that circulates between the carbonator and calciner reactors
k	general deactivation constant for limestones
k_H	fitting parameter to calculate regenerated sorbent activity
N	number of cycles
N_{age}	number of cycles that a natural sorbent needs to go through to reach a value of maximum conversion equal to X'_N
r_N	fraction of calcium that has been cycled between the carbonator and calciner N times
X'_N	maximum carbonation conversion achieved after N cycles after sorbent hydration in the carbonator
X_{ave}	maximum average carbonation conversion attainable by the solids in the carbonator
X_N^H	maximum carbonation conversion achieved by a particle after hydration
X_N	maximum carbonation conversion achieved after N cycles of the solids leaving the calciner
X_r	general residual conversion of limestones after an infinite number of cycles
X_{rH}	fitting parameter to calculate regenerated sorbent activity

What is more, hydration is already a well-established mechanism of reactivation which has been proposed for use with similar Ca-based sorbent materials to capture SO_2 in circulating fluidized bed boilers (CFBC) (see review by Anthony [19]). In this case, the large molar volume of $CaSO_4$ compared to that of CaO, favours pore blockage and the formation of a rich layer of sulphate around the particles or grains of CaO. As a result the diffusion of gaseous species through the $CaSO_4$ layers is slow and therefore the sorbent conversion in CFB systems is low (typically between 30 and 45%). In these cases, hydration can be used to regenerate the used sorbents, as H_2O is able to permeate through the layer of $CaSO_4$ and react with fresh CaO inside the particle to form $Ca(OH)_2$. This process creates cracks in the sulphate layer because the particle swells due to the higher molar volume of $Ca(OH)_2$ compared to that of CaO. As a result, fresh CaO sorbent is exposed to the ambient and this can react further with SO_2 [20].

The hydration process used to reactivate the sorbent for CO_2 capture is different to that of SO_2 because the deactivation mechanisms in the carbonation and sulfation reactions differ. Pore blockage is not so critical in the carbonation reaction unless there is substantial particle shrinkage during calcination [21]. During the carbonation/calcination cycles in a Ca-looping process, the decrease in the carrying capacity of CO_2 is mainly due to the sintering of the sorbent, which reduces the surface area of the solids [6,22,23]. This mechanism is accompanied by the formation of a product layer on the free surfaces of CaO that drastically limits the progress of the carbonation reaction after it has reached a thickness of between 30 and 50 nm [21,24]. Despite the differences in deactivation, the mechanism for reactivating calcium by means of hydration in Ca-looping systems is similar to that of capture by SO_2. The idea is to use the swelling tendency of CaO during hydration to form $Ca(OH)_2$ in order to be able to expose a larger fraction of CaO after the decomposition of $Ca(OH)_2$ in the calciner or in the carbonator. Calcined sorbents after hydration have a higher surface area and pore volume and therefore a greater sorbent carrying capacity.

Hughes et al. [14] conducted an experimental study of this reactivation method with a spent CaO sorbent from a Ca-looping system. They reported an improvement in the capacity of the sorbent to absorb CO_2 during the TGA test and demonstrated that a regenerated sorbent can achieve a conversion of 52% after 20 calcination/carbonation cycles. Fennel et al. [16] proposed the use of water at room temperature to hydrate used sorbents. They applied this method to the regeneration of used lime in a fluidized bed during 30 carbonation/calcinations. After the regeneration step the sorbent was able to achieve a carbonation conversion higher than 50%.

Most of the experimental work carried out has been focussed on the total hydration of sorbents, whilst experiments aimed at analyzing the impact of the partial hydration on deactivated lime are scarce. The effect of partial hydration was studied by Grasa et al. [17] who found that there is a non-linear trend between the level of hydration and the carrying capacity of the regenerated sorbent. Recent studies [25] have shown that more intensive operation conditions are needed to regenerate the sorbent when it has been subjected to a high degree of carbonation, implying that sorbent hydrates more rapidly and to a greater extent in a calcined form. This phenomenon was explained by arguing that the external shell of $CaCO_3$ on CaO surfaces will prevent any reaction between the CaO and the steam. However, in a subsequent work using solids with low carbonation conversions, which are more representative of what might occur in large scale systems, they observed that the external thin shell of $CaCO_3$ did not seem to affect the hydration of the carbonated sorbent very much [26].

The hydration reaction may also be affected by the operation conditions. Some authors claim that the reactivation temperature of the sorbent is a critical parameter, as it determines the degree of activity of the regenerated CaO. Grasa et al. [17] observed that regeneration temperatures higher than 750 °C lead to a decrease in sorbent activity. Similar trends were observed by Wu et al. [27], who completely hydrated their CaO and then reactivated it at different temperatures. They found that high reactivation temperatures (>950 °C) resulted in a sorbent with a lower activity than that of the original CaO.

Another issue to be considered when selecting the operating conditions for a possible reactivation process by means of hydration is the impact that they may have on the mechanical stability of the sorbent. Some researchers [16,17] found that a hydrated sorbent has much poorer mechanical properties and that this may promote the formation of elutriable fines within the system. To avoid the phenomenon of attrition, Materic et al. [28] have proposed a method for reactivating a sorbent that involves the use of steam and a superheated dehydration step at high temperatures (620 °C) in the presence of CO_2. This results in the formation of active $CaCO_3$ that can be reused in the process. The sorbent produced by this method presents better mechanical properties and may reduce the formation of fines.

It is important to put all these variables in perspective, and to consider their impact on the operation of a potential reactivation reactor. This is because, due to the limits of equilibrium, hydration of the sorbent cannot be performed in the calciner or in the carbonator, and so an additional reactor working at lower temperatures is needed. Consequently, the beneficial effects of hydration on the carrying capacity of the sorbent must be weighed against the disadvantages associated with the increase in water and energy consumption entailed by adding a new reactor for hydration. The size of the hydration reactor or hydrator will depend on the degree of hydration required, the residence time of the solids and the flow of the sorbent to be treated. It is obvious that all these variables have to be minimized in order to make the reactivation step economically more interesting than the alternative solutions, such as

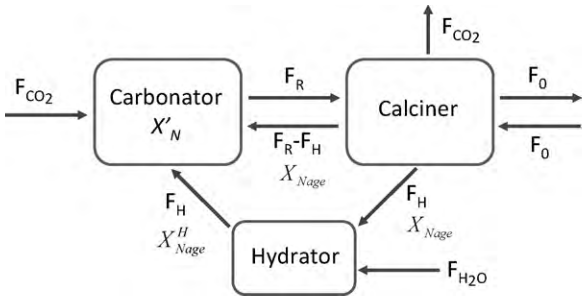

Fig. 1. CO_2 capture process with sorbent reactivation by hydration.

the use of a larger make up flow of fresh limestone. The aim of the present work is to contribute to this analysis by solving the necessary mass balances to establish a relationship between the increase in activity resulting form hydration in continuous mode with the level of reactivation induced in the individual particles and the fraction of total solids circulating through the regeneration reactor. The relationships derived from this will facilitate the selection of suitable reactivation strategies in order to increase the activity of the sorbent and at the same time minimize the consumption of steam in the hydrator and the flow of solids to the reactivation reactor.

2. Mass balance with sorbent reactivation

Fig. 1 shows a process scheme in which a sorbent regeneration by hydration is applied to a Ca-looping cycle. In this process, the solids leaving the calciner are assumed to be composed of only CaO. Other solids such as fuel ash, $CaSO_4$, $CaCO_3$, may be present in this stream, but they are not participating in the CO_2 capture loop and their concentration can be determined from independent mass balances as a function of F_0 and F_R. The CaO leaving the calciner (F_R) is split into two streams, one of which is sent directly to the carbonator, $F_R - F_H$, while the other, F_H, is diverted to a hydrator reactor where CaO reacts with H_2O to form $Ca(OH)_2$ to a certain extent. The stream of hydrated solids is then sent to the carbonator where the $Ca(OH)_2$ decomposes into CaO which is more active than the solids entering the reactivation reactor. The reactivation of the sorbent can be controlled by modifying the degree of hydration which in turn is modified by the operational conditions in the hydrator reactor (residence time, temperature, atmosphere composition, etc.).

Alternative schemes are possible depending on the position of each reactor and the way they are interconnected. The scheme in Fig. 1 is similar to those proposed by other authors [1,5,29], and involves the calcination of $Ca(OH)_2$ in the carbonator and not in the calciner. The advantages of this scheme are that the amount of heat required for calcination will be lower, less attrition of solids should be expected (because the calcination rate will be less severe under these carbonation conditions) and certain benefits can be expected from a partial steam pressure in the carbonator that has been reported to improve sorbent performance when SO_2 is present in the flue gas [30]. However, certain disadvantages should also be mentioned. In the scheme of Fig. 1 the steam is released with the flue gas (whereas if it were released in the calciner it could be captured in the CO_2 purification and compression process). As a result, the partial pressure of CO_2 may decrease significantly in the carbonator if the $Ca(OH)_2$ flow is too large, causing a reduction in the carbonation rates. A decrease in CO_2 partial pressure however does not have the same negative effect in the calciner because the calcination rates will increase with the lower partial pressures of CO_2 and the higher partial pressures of steam.

To sum up, several factors will determine which reactor to use for the calcination of $Ca(OH)_2$ depending on the final process design. Although the analysis that follows applies directly to the scheme in Fig. 1, it could be easily adapted to alternative schemes where the reactivated stream of solids abandoning the hydrator, F_H, returns directly to the calciner.

From Fig. 1, it is clear that the flow of steam entering the hydrator, F_{H_2O}, in the regeneration step is an important process variable that will influence the energy and mass balance of the system. One of the criteria to be considered in designing this process is the need to minimize the amount of steam used in the regeneration reactor with respect to the flow of CO_2 captured in the carbonator and released in the calciner, F_{CO_2}.

Moreover, the calcination of $Ca(OH)_2$ is an endothermic process. If $Ca(OH)_2$ is calcined in the carbonator, the heat has to be supplied by the exothermic reaction between CaO and CO_2. Although the heat used to calcine $Ca(OH)_2$ will be recovered as exothermic heat from the hydration in the reactivation reactor, it must be pointed out that the hydrator works at a relatively low temperatures (<400 °C), which limits the heat recovery efficiency. Although heat integration is beyond of the scope of the present work it is clear that for both heat recovery and H_2O consumption it is important to minimize F_H and F_{H_2O}. This will be one of the main targets of the following analysis.

2.1. Calculation of the average activity of the solids in the CO_2 calcium loop with hydration

As was mentioned above, the maximum carbonation conversion of CaO particles (X_N) in a carbonation–calcination loop without the use of reactivation reactor is reduced due to the deactivation of the sorbent as the number of carbonation and calcination cycles increases (see for example [5,6,31,22]). The decay in the maximum conversion as a function of the cycle number (N) can be calculated using several semiempirical equations. These models calculate the sorbent conversion taking into account the sintering of the sorbent with the number of cycles and the limited thickness of the product layer. In this work, we use an equation that has proven to be valid for a wide range of conditions and many limestones [9]:

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

where k is the deactivation constant, X_r the residual conversion after an infinite number of cycles and N is the number of carbonation and calcination cycles. The values $k = 0.52$ and $X_r = 0.075$ were calculated by adjusting this equation to the results obtained for different limestones over long testing periods [9]. Other authors have used an even larger number of cycles and obtained only slightly different results [30,32,33].

It is important to note that Eq. (1) is only valid for that part of the CaO that undergoes an N number of full carbonation and calcination cycles. As reported elsewhere [34], partial carbonation and calcination has certain effects on the average activity of the materials in the systems, but we shall ignore these effects at this stage in order to focus on the impact of the reactivation introduced by the hydrator reactor in Fig. 1. Moreover, it is not possible to use Eq. (1) directly for particles that have been cycled N times in the system of Fig. 1, because the carrying capacity of CaO, X'_N; has changed to a certain extent due to the perfect mixing with the CaO that passes through the hydrator. However, the "cycle number" for any particle or fraction of CaO can still be determined from the number of calcinations experienced by these particles. The carbonator and the new hydrator reactor do not produce any change in the number of cycles (they remain as N and only change to $N+1$ when the particles go through the calciner again) but the hydrator does produce a certain change in X'_N. In other words, although the maximum carbonation conversion is no longer as indicated by Eq. (1), the fraction of CaO that has been fully carbonated to its maximum level and fully calcined N times, r_N, is still only a function of F_0 and F_R, which allows

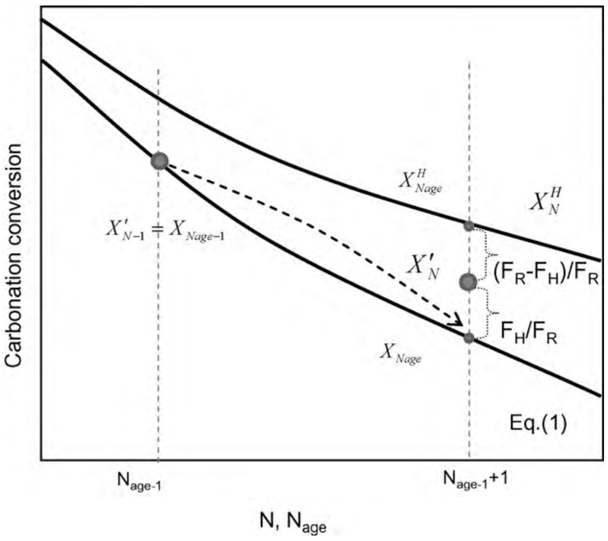

Fig. 2. Graphic representation of the procedure for calculating X'_N.

us to maintain our strategy for calculating the average activity of the solids entering the carbonator, X_{ave}. The definition of the average activity of the materials circulating in the system of Fig. 1 is identical to the definition for a system without a hydration step [35]:

$$X_{ave} = \sum_{N=1}^{N=\infty} r_N X'_N \tag{2}$$

This methodology has been used by other authors to estimate X_{ave} using different assumptions (partial carbonation/calcination [34], doped CaO-based sorbents [36]). If all the reactors in Fig. 1 are ideally mixed fluidized beds, a mass balance yields the fraction of particles that have been cycled N times (r_N) through the calciner:

$$r_N = \frac{F_0 F_R^{N-1}}{(F_0 + F_R)^N} \tag{3}$$

Therefore, once r_N has been defined, the next task is to provide a method for estimating the second term in Eq. (2), the carbonation conversion of particles, X'_N, that have cycled N times through the calciner and that have been partially hydrated on occasionally passing through the hydrator and fully carbonated on passing through the carbonator.

To formulate the necessary mass balances to estimate X'_N, we need to look at the effects of hydration on the individual activity of each fraction of particles. We will assume for convenience the existence of a reactivation function that will enable us to calculate the new carrying capacity, X_N^H, of a certain particle or mass fraction of CaO characterized by a certain maximum activity, X_N, before hydration.

On the basis of the experimental results contained in the references discussed in the Introduction [17] we shall assume that the mathematical form X_N^H is identical to Eq. (1) but with different parameters in order to define the decay of the sorbent's carrying capacity in the subsequent carbonation–calcination cycles. The choice of the parameters, k_H and X_{rH}, allows us to simulate different reactivation scenarios (from full to partial hydration) as will be shown later.

Fig. 2 shows two continuous curves that represent the impact of reactivation on the CaO particles with an original maximum conversion capacity (without reactivation), expressed as X_N, that will change during reactivation to a new maximum conversion capacity of X_N^H.

In order to estimate X'_N for each r_N we will use an induction approach, whereby we set up the necessary mass balances to estimate X'_N from an assumed knowledge of X'_{N-1}. We can therefore complete the infinite sum of Eq. (2) if we know $X_{N=1}$ and the relation between X'_N and X'_{N-1}.

In order to estimate X'_N from X'_{N-1}, we need to define the relevant mass balances as represented in Fig. 2. A particle in its previous cycle, $N-1$ (just before its N calcination) will have reached a carbonation conversion of X'_{N-1}. As was mentioned above, due to the effect of the hydrator, X'_N cannot be calculated directly from the value of N using Eq. (1). However, since we are assuming that X'_{N-1} is known, we can still use Eq. (1) in reverse, in order to calculate an associated cycle number called N_{age} that represents the "age" of the particle taking into account its conversion capacity [37], i.e. the number of cycles that a natural sorbent needs to go through to reach a value of maximum conversion equal to X'_{N-1} in normal conditions.

$$N_{age-1} = \left(\frac{1}{k}\right)\left(\frac{1}{X'_{N-1} - X_r} - \frac{1}{1 - X_r}\right) \tag{4}$$

In other words, if we introduce N_{age-1} in Eq. (1), we obtain a carbonation conversion, $X_{N_{age-1}}$, that is equal to that of the particles that have cycled $N-1$ times ($X'_{N-1} = X_{N_{age-1}}$). The reason for introducing the concept of N_{age} into this analysis is because it allows us to calculate the loss of activity of a particle during one additional calcination step, by simply increasing the cycle number to N_{age} from N_{age-1}. Therefore, if a particle has been cycled $N-1$ times, it will have a value of N_{age-1} before it enters the calciner, where it will experience a drop in activity characteristic of an increase in $N_{age} = N_{age-1} + 1$. The corresponding activity or maximum carbonation conversion after calcination, $X_{N_{age}}$, can then be calculated using Eq. (1) with N_{age}. If the particle is directed to the carbonator without passing through the hydrator (i.e. it is part of the solid stream $F_R - F_H$), its maximum carbonation conversion in the carbonator will be $X_{N_{age}}$. But, if the particle is sent to the carbonator via the hydrator, its activity will be upgraded from $X_{N_{age}}$ to $X^H_{N_{age}}$ according to the reactivation function X_N^H defined above. With these definitions we know the activities of particles circulating through the system of Fig. 1 and we can then set up the mass balances taking into account the solid flows in order to estimate X'_N:

$$X'_N = X_{N_{age}} \frac{(F_R - F_H)}{F_R} + X^H_{N_{age}} \frac{F_H}{F_R} \tag{5}$$

where both $X_{N_{age}}$ and $X^H_{N_{age}}$ are estimated from a value of X'_{N-1} as indicated in the previous paragraph.

As for $X'_{N=1}$, we are assuming that $X_{N_{age=1}} = X^H_{N_{age=1}}$ (as given by Eq. (1)) because this is consistent with the experimental evidence which indicates that the very active particles derived from the first cycle experience little additional activation as a result of hydration. However, the calculation approach proposed can still be applied for hydration conditions where $X^H_{N_{age=1}} \neq X_{N_{age=1}}$. In this case, if the maximum carbonation conversion of the hydrated fresh calcined lime is known, $X'_{N=1}$ can be calculated by using Eq. (5) and introducing $X_{N_{age=1}}$ and $X^H_{N_{age=1}}$.

The calculation procedure outline above allows X_N and r_N to be calculated from $N = 1$, and hence, the average carbonation conversion in the carbonator can be calculated by using Eq. (2). The summation of Eq. (2) is straightforward because for typical values of F0/FR higher than 0.001 it is usually enough to consider values of N of around 10,000 in order to account for more than 99.9% of the particles in the system and obtain a very good estimate of X_{ave}. It is then possible to analyze the effects of the key operation conditions, F_{H_2O}, F_H, F_R, F_0, on the maximum carbonation conversions, and the consequences for the different reactivation strategies.All that

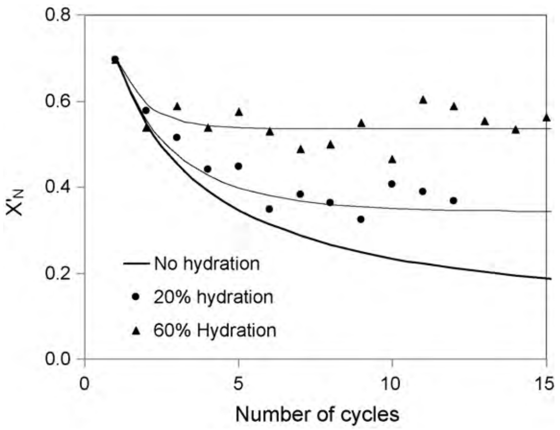

Fig. 3. Comparison of the experimental results reported by Grasa et al. [17] and model predictions (Eq. (5) with $F_H/F_R = 1$) for two hydration conditions, 20 and 60%.

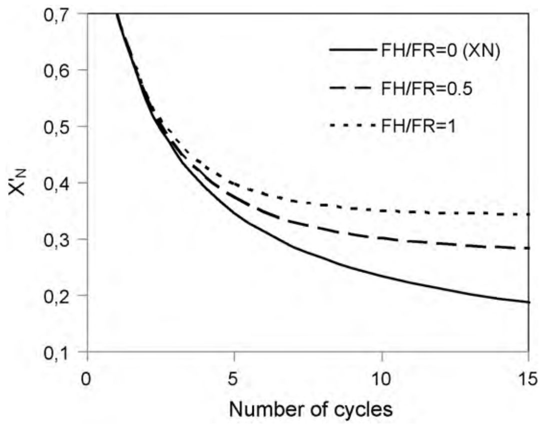

Fig. 4. Effect of F_H on maximum carbonation conversion X'_N achieved by solids after hydration at 20%.

remains to be done is to determine by means of suitable laboratory experiments X_N^H (top line of Fig. 2).

Unfortunately, we have not been able to find in the literature suitable data that can be directly fitted to the X_N^H curve. The experimental curve of X_N^H can be constructed on the basis of the improvement in sorbent carrying capacity of many original samples of sorbent with different starting carrying capacities. This should be done in different sets of operating conditions (hydration atmosphere, temperature, pressure, reaction time, etc.). In the absence any direct method of determining X_N^H, we attempted to re-interpret published data on hydration and to put them in a form suitable for adjusting them to the curve X_N^H on the basis of sufficient experimental evidence to support the analysis presented in this work. As pointed out above, the function adopted for X_N^H was that of Eq. (1), and therefore, the definition of X_N^H requires the definition of parameters k_H and X_{rH}. The source of the experimental data was a previous study on hydration in a TGA of a high purity limestone [17]. The thermogravimetric equipment (TGA) used during the experiments has been described elsewhere [9]. The reacting gas mixture (CO_2, O_2/air; air/steam) was regulated by mass flow controllers and fed into the bottom of the quartz tube. Temperature and sample weight were continuously recorded in a computer. The routine of the experiments was calcination of the sample (in air at 900 °C for 5 min), a reactivation stage (hydration with steam, pH_2O 0.5 atm and 400 °C in air) and carbonation (pCO_2 0.1 atm and 650 °C for 5 min).

The key assumption for deriving k_H and X_{rH} is that particles in these TGA experiments are equivalent to particles with a value of $F_H/F_R = 1$ (i.e. 100% of the solids cycling in both systems undergo hydration). Therefore, the carbonation conversion of the fraction of solids cycled N times, X'_N, will be equivalent to the maximum carbonation conversion determined in the TGA after hydration, when the solids are hydrated between each calcination/carbonation cycle ($X'_{N_{age}} = X^H_{N_{age}}$ when $F_H/F_R = 1$ according to Eq. (5)). Thus, k_H and X_{rH} can be calculated as fitting parameters in the calculation procedure explained above to calculate X'_N with Eq. (5) for $F_H = F_R$. Fig. 3 compares the results of this analysis, using k_H and X_{rH} as adjustable parameters for hydration conversions of 0.20 ($k_H = 0.63$; $X_{rH} = 0.15$) and 0.60 ($k_H = 1.39$; $X_{rH} = 0.36$), and shows the experimental maximum carbonation and those predicted with the model (solid line). As can be seen, there is reasonable agreement between the theoretical and experimental results at both degrees of hydration. It should also be noted that the X'_N curves for these degrees of hydration show stable values with a relatively small number of cycles. This corresponds to the point where the gain in carrying capacity during hydration becomes equal to the loss of activity during each carbonation/calcination cycle.

Finally, Fig. 4 represents an example of the three relevant functions discussed above. They define as a function of the number of full carbonation calcination cycles the maximum conversion achieved in the absence of hydration, X_N, and the maximum conversion achieved by solids in the continuous process scheme of Fig. 1 as a function of X_N^H and the fraction of solids F_H/F_R passing through the hydrator reactor X'_N. In the scenario where no solids are diverted through the hydrator, $F_H/F_R = 0$, there is no sorbent reactivation and the carbonation conversion of solids can be calculated directly by means of Eq. (1) ($X'_N = X_N$). However, when a stream of solids is passed through the hydrator, there is an increase in activity for each fraction of particles cycled N times, and this activity increases further with F_H.

3. Effect of sorbent hydration on the CO_2 capture process

To evaluate the effect of the degree of hydration and the amount of solids sent to the hydrator, F_H, on the system of Fig. 1, two different scenarios were analyzed using the X_N^H curves determined for 0.20 and 0.60 of sorbent hydration and compared with equivalent scenarios where $F_H/F_R = 0$ ($X'_N = X_N$). The results are presented in Fig. 5, where X_{ave} was calculated using the procedure explained in the previous section, using Eq. (4) for a fixed value of F_R. As can be seen from this figure, when there is no hydration ($F_H/F_R = 0$), X_{ave} is directly linked to F_0/F_R and the average activity of the solids in the carbonator can only be increased by adding fresh sorbent to the system. However, as discussed in the introduction, the purpose of the hydration process is to reduce the consumption of fresh limestone required to achieve a certain activity X_{ave}. As can be seen in Fig. 5, X_{ave} can be increased greatly by hydrating the sorbent instead of by adding fresh limestone to the system. The higher the amount of solids diverted to the hydrator, F_H, the higher the X_{ave} value and the amount of CO_2 that can be captured in the carbonator for a fixed value of solids circulation rate between the carbonator and calciner (F_R). However, it should be noted that the effect of F_H on X_{ave} is less pronounced for high values of F_0/F_R. As mentioned before, hydration tends to be not very effective for regenerating active sorbents whereas it is highly effective for increasing the activity of very deactivated solids. Therefore, for high values of F_0/F_R, the fraction of active sorbent in the system increases as a result of increased fractions of particles with low cycle numbers, and in these conditions the hydration is accordingly less effective.

Comparison of the two graphs in Fig. 5 also highlights an important effect that the hydration degree has on the X_{ave} computed for identical conditions of F_H, F_0 and F_R. If we compare the results obtained for the two hydration degrees of 0.2 and 0.6, it can be seen that the increase in activity for a hydration of 0.6 is higher than that

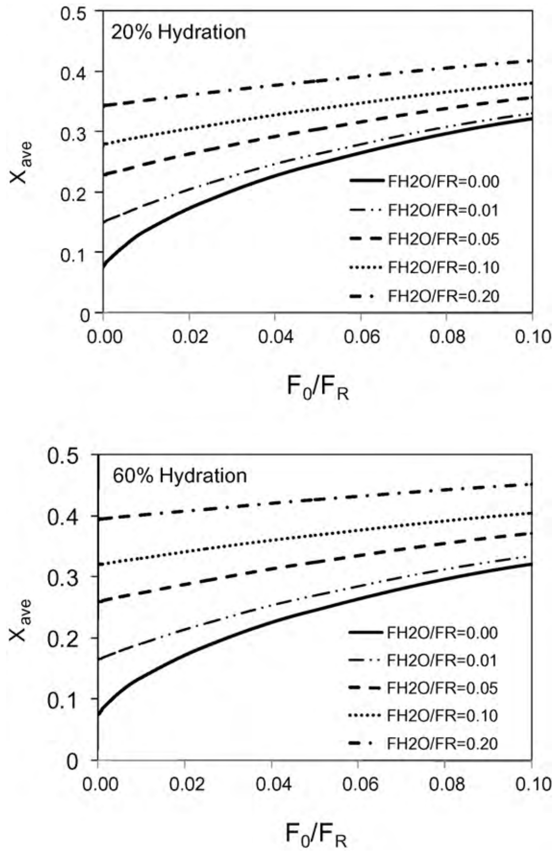

Fig. 5. Effect of F_H and F_0 on X_{ave} for both degrees of hydration.

of 0.2 for the same amount of steam consumption (F_{H_2O}/F_R). This shows that higher degrees of hydration can lead to greater reactivation. This can be explained by assuming that steam will react preferably with active lime. If a small amount of steam is used in the hydration reactor, this will react preferably with the active part of the sorbent, which will hardly undergo any reactivation as it is already active for CO_2 capture, and so less H_2O will be available to react with the non-active CaO. However, if more steam is added, the reaction with non-active lime will take place to a larger extent and the steam will serve to regenerate the deactivated part of the sorbent more efficiently. Besides having an impact on sorbent reactivation, higher degrees of hydration may serve to reduce the amount of solids sent to the hydrator (F_H) in order to obtain a specific value of X_{ave}. This would help to reduce the size the regeneration reactor. It should also be noted that for the cases analyzed in this work, for a fixed value of steam consumption (F_{H_2O}/F_R), the amount of solids sent to the hydrator is three times smaller if the sorbent is hydrated to a degree of 0.60 instead of a 0.2.

In a Ca-looping CO_2 capture system, a fraction of the CO_2 fed into the carbonator may not be captured and may be released with the flue gas. The ratio between the CO_2 fed into the carbonator (F_{CO_2}) and the CO_2 captured is defined as CO_2 capture efficiency (E_C):

$$E_C = \frac{F_R X_{ave}}{F_{CO_2}} \tag{7}$$

To analyze the effect of sorbent hydration on the performance of the CO_2 capture process, Fig. 6 shows the capture efficiency for a fixed solids circulation of 5 mol CaO/mol CO_2 between carbonator and calciner. These results correspond to a hydration degree of 0.60 and three different levels of steam consumption, 0.03, 0.15 and 0.30 mol H_2O/mol CO_2. As can be seen from this figure, if no steam is added, a solids circulation of 5 mol CaO/mol CO_2 is not enough to achieve high capture efficiencies (>80%), unless a high make up flow is used ($F_0/F_{CO_2} > 0.08$) or unless the solid circulation (F_R) is increased. However, for low values of F_0/F_{CO_2}, high values of E_C can be achieved by introducing steam into the hydrator. It is noteworthy that even if no fresh limestone is added to the system ($F_0/F_{CO_2} = 0$), capture efficiency can be as high as 0.85 for a solid circulation rate of 5 mol CaO/mol CO_2, if a 0.3 mol of steam/mol CO_2 is fed into the hydrator. However in real systems, due to the ash and/or sulphur content of the fuel used in the calciner, a flow of purge can be expected to keep the inventory of solids in the system constant or to remove any $CaSO_4$. In such a situation, a compromise between a minimum value of F_0, to purge the system, and a flow of steam to increase X_{ave} must be adopted.

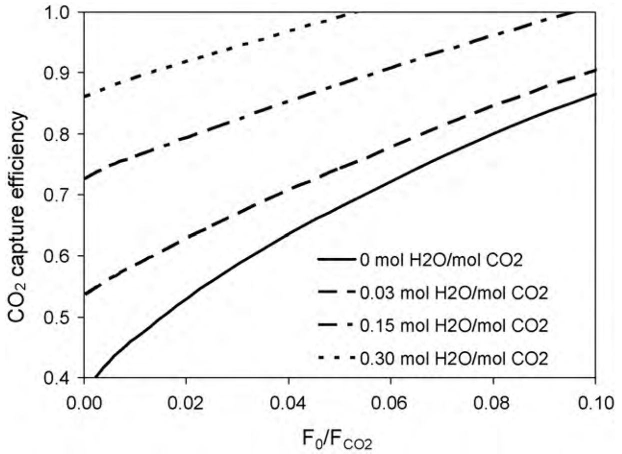

Fig. 6. Effect of steam consumption on capture efficiency for a solids circulation of 5 mol Ca/mol CO_2 and a hydration degree of 60%.

Besides having an effect on the CO_2 balance, the internal circulation rate (F_R) has an influence on other aspects of the system, such as the energy balance (i.e. heat requirements in the calciner). For this reason, it is important to keep F_R at reasonable low values. In accordance with Eq. (7), once the CO_2 capture parameters have been fixed (E_C and F_{CO_2}), there is a link between the different mass flows involved in the system (F_0, F_R and F_H). To illustrate these effects, Fig. 7 shows the relation between molar steam consumption (F_{H_2O}/F_{CO_2}) and the solids circulation for different make up flows and a fixed capture efficiency of 0.9. It can be seen that for a fixed value of F_0/F_R, the solids circulation can be reduced by means of sorbent hydration. As was mentioned before, the effect of

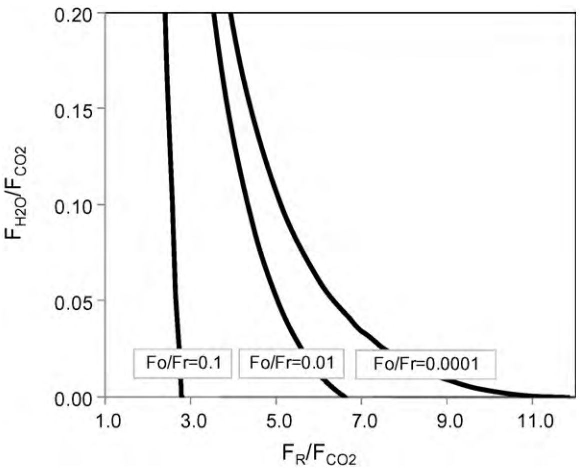

Fig. 7. Effect of steam consumption on solid circulation rate between reactors for a capture efficiency of 0.9 using a hydration degree of 0.6.

sorbent hydration on F_R is higher for low F_0/F_R ratios. For high make up flows, the activity of the solids in the system (X_{ave}) is influenced more by the addition of fresh limestone. On the other hand, for low make up flows, the solids in the system exhibit a low activity. In this case, sorbent hydration is an effective method to increase X_{ave} and thereby reducing the solids circulation requirements between reactors.

4. Conclusions

A process for integrating sorbent hydration into a Ca-looping cycle has been analyzed by adding a new reactor to the CO_2 capture loop and solving the associated mass balances for the three interconnected reactors. The main variables that influence the level of sorbent regeneration are the mass flow of solids sent to the hydrator and the degree of hydration. The solution of the mass balances taking into account the sorbent decay curves and the functions for calculating the fraction of particles in the system calcined a given number of times makes it possible to evaluate the impact of hydration on sorbent activity and capture efficiency. Two different scenarios of partial hydration were analyzed (20 and 60%). When a hydrator reactor is integrated into the CO_2 capture process, the average activity of the solids circulating in the system can be increased by using steam instead of fresh limestone. The results obtained in this work indicate that steam is more efficient when the sorbent is hydrated to a high degree. In the scenarios analyzed in this work, the activity recovered by the sorbent after hydration can be 45% higher if the sorbent is hydrated to 0.6 instead to 0.2. This means that for a given value of steam consumption, it is more suitable to divert a smaller flow of solids to the hydrator and to regenerate them to a higher level (up to 0.6) than to use a lower hydration level (0.2) and a larger solids flow. On the other hand, improvement in average sorbent activity by means of hydration is more pronounced when the system is working with highly deactivated solids, which is characteristic of situations where a low make up flow of fresh limestone is used.

Acknowledgement

This work is partially funded by the European Commission (FP7-CaOling project).

References

[1] D.P. Harrison, Sorption-enhanced hydrogen production: a review, Ind. Eng. Chem. Res. 47 (2008) 6486–6501.

[2] E.J. Anthony, Solid looping cycles: a new technology for coal conversion, Ind. Eng. Chem. Res. 47 (2008) 1747–1754.

[3] J. Blamey, E.J. Anthony, J. Wang, P.S. Fennel, The calcium looping cycle for large-scale CO_2 capture, Prog. Energy Combust. Sci. 36 (2010) 260–279.

[4] M. Haines, IEAGH high temperature looping cycle network, IEAGHG: Greenhouse Issues 96 (2010) 4.

[5] G.P. Curran, C.E. Fink, E. Gorin, CO_2 acceptor gasification process. Studies of acceptor properties, Adv. Chem. Ser. 69 (1967) 141–161.

[6] R. Barker, Reversibility of the reaction $CaCO_3 = CaO + CO_2$, J. Appl. Chem. Biotechnol. 23 (1973) 733–742.

[7] J.C. Abanades, E.S. Rubin, E.J. Anthony, Sorbent cost and performance in CO_2 capture systems, Ind. Eng. Chem. Res. 43 (2004) 3462–3466.

[8] N. Rodriguez, M. Alonso, G. Grasa, J.C. Abanades, Process for capturing CO_2 arising from the calcination of the $CaCO_3$ used in cement manufacture, Environ. Sci. Eng. 42 (2008) 6980–6984.

[9] G.S. Grasa, J.C. Abanades, CO_2 capture capacity of CaO in long series of carbonation/calcination cycles, Ind. Eng. Chem. Res. 45 (2006) 8846–8851.

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

[11] J.C. Abanades, M. Alonso, N. Rodriguez, B. González, G. Grasa, R. Murillo, Capturing CO_2 from combustion flue gases with a carbonation calcination loop. Experimental results and process development, Energy Proc. 1 (2009) 1147–1154.

[12] A. Charitos, C. Hawthorne, A.R. Bidwe, H. Holz, T. Pfeifer, A. Schulze, D. Schlegel, A. Schuster, G. Scheffknecht, Parametric study on the CO_2 capture efficiency of the carbonate looping process in a 10 kW dual fluidized bed, in: Proceedings of the 20th International Conference on Fluidized Bed Combustion, Springer, Xi'an, P.R. China, 2009, pp. 753–758.

[13] P. Lisbona, A. Martinez, Y. Lara, L.M. Romeo, Integration of carbonate CO_2 capture cycle and coal-fired power plants. A comparative study for different sorbents, Energy Fuels 24 (2010) 728–736.

[14] R.W. Hughes, D. Lu, E.J. Anthony, Y. Wu Y, Improved long-term conversion of limestone-derived sorbents for in situ capture of CO_2 in a fluidized bed combustor, Ind. Eng. Chem. Res. 43 (2004) 5529–5539.

[15] V. Manovic, E.J. Anthony, Steam reactivation of spent CaO-based sorbent for multiple CO_2 capture cycles, Environ. Sci. Technol. 41 (2007) 1420–1425.

[16] P.S. Fennell, J.F. Davidson, J.S. Dennis, A.N. Hayhurst, Regeneration of sintered limestones sorbents for the sequestration of CO_2 from combustion and other systems, J. Energy Inst. 80 (2007) 116–119.

[17] G. Grasa, R. Murillo, M. Alonso, B. González, N. Rodriguez, J.C. Abanades, Steam reactivation of CaO-based natural sorbents applied to a carbonation/calcination loop for CO_2 capture, in: 4th International Conference on Clean Coal Technologies, Dresden, Germany, 2009.

[18] G.P. Curran, Preparation of carbon dioxide acceptors by the melt process, Patent U.S. No. 3,516,808 (1970).

[19] E.J. Anthony, E.M. Bulewicz, L. Jia, Reactivation of limestone sorbents in FBC for SO_2 capture, Prog. Energy Combust. Sci. 33 (2007) 171–210.

[20] K. Laursen, W. Duo, J.R. Grace, C.J. Lim, Characterization of steam reactivation mechanisms in limestones and spent calcium sorbents, Fuel 80 (2001) 1293–1306.

[21] D. Alvarez, J.C. Abanades, Pore-size and shape effects on the recarbonation performance of calcium oxide submitted to repeated calcination/recarbonation cycles, Energy Fuels 19 (2005) 270–278.

[22] S.K. Bathia, D.D. Perlmutter, Effect of the product layer on the kinetics of the CO_2-lime reaction, AIChE J. 29 (1983) 79–86.

[23] J.C. Abanades, D. Alvarez, Conversion limits in the reaction of CO_2 with lime, Energy Fuels 17 (2003) 308–315.

[24] 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.

[25] 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.

[26] V. Manovic, D. Lu, E.J. Anthony, Steam hydration of sorbents from a dual fluidized bed CO_2 looping cycle reactor, Fuel 87 (2008) 3344–3352.

[27] Y. Wu, J. Blamey, E.J. Anthony, P.S. Fennel, Calcium looping cycles-sorbent particle size change and steam reactivation, in: 1st Meeting of IEAGH High Temperature Looping Cycle Network, 2009.

[28] S. Smedley, V. Materic, C. Henderson, Gas separation process, Patent Cooperation Treaty Application, No. WO0-148334 (2009).

[29] F. Zeeman, Effect of steam hydration on performance of line sorbent for CO_2 capture, Int. J. Greenhouse Gas Control 2 (2008) 203–209.

[30] P. Sun P, J.R. Grace, C.J. Lim, E.J. Anthony, Investigation of attempts to improve cyclic CO_2 capture by sorbent hydration and modification, Ind. Eng. Chem. Res. 47 (2008) 2024–2032.

[31] A. Silaban, D.P. Harrison, High temperature capture of carbon dioxide: characteristics of the reversible reaction between CaO(s) and CO_2(g), Chem. Eng. Commun. 137 (1995) 177–190.

[32] A.I. Lysikov, A.N. Salanov, A.G. Okunev, Change of CO_2 carrying capacity of CaO in isothermal recarbonation–decomposition cycles, Ind. Eng. Chem. Res. 46 (2007) 4633–4638.

[33] J. Wang, E.J. Anthony, A common decay behavior in cyclic processes, Chem. Eng. Commun. 194 (2007) 1409–1420.

[34] N. Rodriguez, M. Alonso, J.C. Abanades, Average activity of CaO particles in a calcium looping system, Chem. Eng. J. 156 (2010) 388–394.

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

[36] Y. Li, C. Zhao, H. Chen, L. Duan, X. Chen, Cyclic CO_2 capture behaviour of $KMnO_4$-doped CaO base sorbents, Fuel 89 (2010) 642–649.

[37] G. Grasa, J.C. Abanades, E.J. Anthony, Effect of partial carbonation on the cyclic CaO carbonation reaction, Ind. Eng. Chem. Res. 48 (2009) 9090–9096.