

Evaluation of CO₂ carrying capacity of reactivated CaO by hydration

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ABSTRACT. Steam hydration has been proposed as a suitable technique for improving the performance of CaO as a regenerable sorbent in CO₂ capture systems. New hydration experiments conducted in this study, confirm the reported improvements in the capacity of sorbents to carry CO₂. An examination of the textural properties of the sorbent after hydration and mild calcination revealed a large increase in the area of reaction surface and the formation of a fraction of pores ≈ 20 nm diameter that enhance the CO₂ carrying capacity and increase the carbonation reaction rate. However, these changes in textural properties also lead to lower values of crushing strength as measured in the reactivated particles. Experiments conducted with a high hydration level of the sorbent (Ca molar conversion to Ca(OH)₂ of 0.6) in every cycle produced a sixfold increase in the sorbent residual CO₂ carrying capacity. This improvement has been estimated to be achieved at the expense of a very large consumption of steam in

the system (about 1.2 mol of steam per mol of captured CO₂). The trade off between the improvements in CO₂ capture capacity and steam consumption is experimentally investigated in this work, it being concluded that there is need to design a comprehensive sorbent reactivation test that takes into account all of the hydration reactivation process.

KEYWORDS Ca-looping, CO₂ capture, sorbent reactivation, steam hydration

INTRODUCTION

Ca-looping is a rapidly developing CO₂ capture technology both in postcombustion and pre-combustion CO₂ systems (see recent reviews¹⁻³). The reaction of a CaO-based sorbent with CO₂ to form CaCO₃ and the reverse calcination reaction (mainly in a pure CO₂ or CO₂/H₂O atmosphere) are the basis of all Ca-looping systems. Natural, low price, CaO precursors such as limestones and dolomites should be in principle suitable sorbents for implementing this technology. However, the capture capacity of these CaO sorbents is known to decay rapidly with the number of calcination/carbonation cycles (see for example^{4, 5}) and for this reason their evolution as a function of different variables has been widely investigated (see compilation of previous works^{2, 3, and 6}). Various attempts have been made to model the decay in sorption capture capacity by subjecting natural limestones to a number of cycles and calcination conditions.⁷⁻¹¹ Equation (1) has been applied in previous works to describe the evolution of the maximum sorbent CO₂ capture capacity, X_N, with the number of calcination/carbonation cycles. It has been found that the decay of sorbent carrying capacity with the increasing number of reaction cycles can be fairly described for an important variety of limestones and reaction conditions when a deactivation constant k of 0.52 and a sorbent residual molar conversion X_r of 0.075 are used.⁹

$$X_N = \frac{1}{\frac{1}{(1-X_r)} + kN} + X_r \quad k=0.52, X_r=0.075 \quad (T_{\text{calc}} < 950 \text{ }^\circ\text{C}, t_{\text{calc}} < 20 \text{ min}) \quad (1)$$

It has been demonstrated in recent experimental pilot testing¹²⁻¹⁴ that the Ca-looping system can be efficiently operated using sorbents with a molar carrying capacity very close to the residual activity of natural sorbents. However, it would be better if such processes were able to operate with solids that had a higher CO₂ carrying capacity, because then the reactors would require much lower solid circulation rates and/or lower solid inventories. Any reduction in sorbent circulation requirements for a given fresh sorbent make-up flow and CO₂ capture efficiency, would reduce the fuel requirements in the calciner unit¹⁵, and this would translate into a greater overall energy efficiency.¹⁶ It has been recently demonstrated¹⁷ that the optimum heat integration of the Ca-looping process in the steam cycle of a power plant (requiring minimum energy consumption in the CO₂ compressor and in the air separation unit that supplies O₂ to the calciner) would not require sorbents with CO₂ molar carrying capacities higher than 0.2-0.3. However, this would be still far from the residual value of sorbents derived from natural precursors (that for the majority of natural sorbents range between 0.05 and 0.12 moles CO₂/mol CaO) making it necessary to use very large make up flows of fresh limestone, that would only be economically viable if there was a large consumption of CaO in the proximity of the power plant (e.g. cement industry). Therefore, there is still scope for the design of sorbent improvement processes in Ca-looping systems, as long as they do not compromise the low cost and low energy penalty inherent in these CO₂ capture processes.

There is a wide range of studies on different methods to improve sorbents for Ca-looping systems and/or to include sorbent reactivation techniques (see recent review).³ One of the most promising low cost methods to enhance sorbent performance in Ca-looping systems is the hydration of deactivated material.¹⁸⁻²⁶ The idea of reactivating CaO particles for Ca-looping processes by hydration was first proposed during the development of the Acceptor Gasification Process in the 70s.²⁷ Furthermore, hydration is already a well-established mechanism of reactivation used for similar Ca-based sorbent materials in SO₂ capture applications in circulating fluidized bed boilers (CFBC) (see review).²⁸ In this case, H₂O permeates through the CaSO₄ layer formed and then it reacts with fresh CaO to form Ca(OH)₂. The higher molar volume of this compound, with respect to original CaO, creates cracks on

the sulphate layer thereby exposing the fresh CaO so that continues to react with SO₂.²⁹ Although the sorbent deactivation mechanism for CO₂ capture applications is different to SO₂ capture, the reactivation mechanism by hydration is similar in both cases. The swelling tendency of CaO during hydration helps to expose a greater surface area of CaO to the atmosphere once the Ca(OH)₂ has decomposed. Calcination of the sorbent after hydration regenerates part of its microstructure increasing its surface area and pore volume and as a result its CO₂ carrying capacity is increased.^{20, 26}

Various reactivation conditions for steam hydration have been reported: high pressure steam,¹⁹⁻²¹ atmospheric pressure steam,²³⁻²⁶ steam under atmospheric pressure in a mixed environment of steam and CO₂³⁰ or even with moist air²² or liquid water.²⁵

In addition to the exceptional improvements in CO₂ carrying capacity reported in the laboratory scale works referred to above, there are several wider issues to consider when designing a reactivation process using steam hydration linked to a Ca-looping cycle. The hydration reaction of CaO, which is exothermic, can progress in pure steam at atmospheric pressure up to 520°C, but has been reported to occur at relevant rate at temperatures up to 400 °C at atmospheric pressure.³¹ Therefore, the hydration of the sorbent cannot be performed in the calciner or the carbonator units and an additional reactor operating at lower temperatures is needed. The inclusion of a hydration reactor in the process may affect the efficiency penalty associated to a Ca looping system for CO₂ capture. The generation of steam to reactivate the sorbent requires an energy consumption and also the decomposition of Ca(OH)₂ is an energy demanding process. The energy consumed to decompose the Ca(OH)₂ could be partially recovered during hydration as it is an exothermic process. However, the hydrator reactor will work at low temperature (probably below 400 °C) making difficult to integrate this energy recovered into a steam cycle. Moreover, the steam released due to the decomposition of Ca(OH)₂ to CaO may affect the design or operation of the reactors in the Ca-looping cycle (carbonator and calciner) as the composition and flow of the gas streams would be altered.

An attempt to integrate present knowledge on the improvement of sorbent performance by hydration with accepted methods of solving the mass balances of the different populations of particles circulating

in a general Ca-looping system has been published recently.³² In this publication, it was shown that in order to optimize the design of the process, more experimental information is needed on ways to improve sorbent carrying capacity by hydration under reasonable conditions and reaction times. The objective of the present work is to expand the database of relevant experimental data so as to assess the possibility of reactivation by hydration on the basis of experimental results obtained using materials and experimental conditions that are suitable for the design of continuous hydration-incorporated Ca-looping systems. To this end changes in CO₂ carrying capacity, reaction rate and particle strength after hydration using different number of cycles, hydration levels and calcination conditions have been studied.

EXPERIMENTAL TECHNIQUES

Cyclic calcination/hydration/carbonation tests were carried out using a limestone ordinary from the North of Spain with a narrow particle size cut of 0.4-0.6mm. The limestone was analysed through an ICP-OES Spectrometer and presented a residue after loss on fusion of 56.65% by weight mainly composed by CaO (93.8% wt), MgO (2.23% wt) and SiO₂ (2.24% wt). The thermogravimetric equipment (TGA) employed for the experiments has been described elsewhere.⁹ The reacting gas mixture (CO₂/air; air/steam) was fed into the bottom of a quartz tube reactor placed into a furnace. The gas flow was regulated by mass flow controllers and the steam was generated by external electric heating of the water flow set by a liquid mass flow controller. Total gas flow was set at 4.16e⁻⁶ Nm³/s. The temperature and sample weight were continuously recorded on a computer. The experimental routine consisted of calcination of 10 mg of sample (in air at 900 °C for 5 min), a reactivation stage (hydration with steam, p_{H₂O} at 50 kPa and 380 °C in air) and carbonation (p_{CO₂} at 10 kPa in air and 650 °C for 5 min). There were two intermediate stages to adequate the temperature of the sample to the reaction temperature: a first stage to cool down the sample from calcination to hydration temperature and a second stage to heat up the reactivated sample to carbonation temperature, both in air. The reactivated sample was completely dehydrated during the heating up period previous to carbonation.

The use of this piece of equipment allows accurate control of the sorbent reactivation and enables different aspects of the process such as the level of sorbent hydration and hydration rates as a function of the number of calcination/carbonation cycles to be evaluated. The equipment and technique also allow the inclusion of a reactivation stage in every cycle if desired. The experimental routine was altered on occasions, as will be seen below, to accommodate experiments where the reactivation stage was carried out once every 5 cycles approximately.

In order to analyze the effect of the level of CaO hydration on its CO₂ carrying capacity and reactivity, some samples were examined by means of textural analysis. Mercury porosimetry (Quantachrome Pore Master porosimeter) was used to estimate the pore volume and the pore-size distribution and N₂ adsorption (Micromeritics ASAP2020) at 77 K was used to calculate the sorbent surface area by applying the Brunauer, Emmett and Teller equation.³³ The crushing strength of reactivated and non-activated particles was also measured in order to assess the influence of hydration on the mechanical properties of the particles. To do so, a simple laboratory test was conducted to two different batches of particles: a first batch of non-activated particles and a second batch formed by reactivated particles. The first batch of particles was calcined and then carbonated (following the typical calcination/carbonation cycle described in the experimental part) and around 20 particles were crushed at every stage in the cycle. The second batch of particles was calcined, reactivated up to 80% hydration, and finally carbonated. The two batches of samples exhibited very similar final carbonation conversions. As in the first batch, the crushing strength of 20 particles was measured at the end of every reaction stage (raw limestone, calcined, hydrated and carbonated).

RESULTS

Figure 1 shows a typical example of raw experimental data obtained as weight vs. time at different reaction stages, i.e. calcination-hydration-carbonation. In the experiment represented in Figure 1, there are five cycles that include a reactivation stage by steam hydration between calcination and carbonation of the sorbent. The reactivation of the sorbent takes place from cycle 2 to 6 inclusive (marked in the

figure by arrows). During the next 15 cycles, the experimental routine changes to calcination of the sample followed by carbonation with the final 3 cycles including again a reactivation stage. From the Figure 1 it can be seen that sorbent capture capacity can be maintained during cycling when a reactivation stage is included at every cycle. It can also be observed, in agreement with the literature, that when the sorbent is no longer be reactivated, its capture capacity decreases following the typical decay trend observed for natural sorbents.^{23, 25, 26}

Figure 1.

Figure 1 also shows that the incorporation of a reactivation stage by steam hydration leads to a recovery of sorbent activity even when the sorbent has not been reactivated for several cycles. Indeed, most of the experimental work on reactivation by steam hydration in the literature is based on steam reactivation of samples that have previously experienced a given number of calcination/carbonation cycles in a TGA equipment^{18, 25, 26} or even after being used in a small fluidised bed²² or a pilot plant scale Ca-looping system.^{23, 24} In contrast with these general trends Sun et al. (2008)²⁵, reported the poor performance of hydrated samples in some tests where the Ca(OH)_2 formed after hydration was exposed to temperatures up to 850 °C prior to carbonation. It should be pointed out that during our experiments, as in Figure 1, the temperature was increased after the hydration step under inert atmosphere before the carbonation reaction started at 650 °C. Some experiments that were designed to test the effect of the Ca(OH)_2 calcination temperature revealed that when the sample was exposed to temperatures above 750°C right after hydration the benefits of the reactivation process disappeared and carbonation conversion reverted to what it had been in the cycle prior to hydration. This is consistent with the results referred to above²⁵ and shows that the solids should be directed to the carbonation unit after the hydration step rather than to the calciner. Note that there is a negative side to this approach if the solids circulating in the loop have experience substantial hydration, since the steam released during the decomposition of Ca(OH)_2 would reduce the partial pressure of the CO_2 in the carbonator, which is the driving force for the absorption of CO_2 by CaO .

In this work, we have carried out a series of reaction experiments like the one in Figure 1, and have achieved different levels of hydration for each sample using different number of cycles and hydration steps with different frequencies. The experimental results from these series will be presented in the discussion section. However, it can be seen from Figure 1, that the hydration of CaO is able to to reactivate the particles towards carbonation.

The changes in sorbent performance after hydration are probably due to the dramatic changes in the texture of the materials resulting from the hydration and subsequent calcination of Ca(OH)₂. Some of the reactivated samples were subjected to textural analysis by mercury porosimetry and N₂ adsorption in order to estimate the pore volume, pore-size distribution and to calculate the surface area. These samples were dehydrated previously to textural analysis. Some results are presented in Figure 2, which includes Hg porosimetry data from a sample of calcined limestone (1st cycle calcined), a second sample that had experienced 5 calcinations (named 5th cycle calcined) and from two samples of this material after hydration up to different levels of molar conversion to Ca(OH)₂, (named X_H in the text). An interesting feature in the data presented in Figure 2 is that the reactivated samples (both 60% and 20% hydrated) have a large number of pores below 50nm. Both samples present a substantial pore volume made up of ≈ 20 nm pores that must have been originated from within the process, as this size is even lower than the typical pore size measured in samples calcined for the first time. The least reactivated sample presents a bi-modal distribution, with narrow pores below 50 nm and a considerable fraction of larger pores typical of multi-cycled CaO particles.³⁴

Figure 2.

As expected, the sample with the lowest surface area ($S_g=6 \text{ m}^2/\text{g}$ BET surface) was that corresponding to the 5th cycle of calcination. Sorbent reactivation with steam increased the S_g to $13 \text{ m}^2/\text{g}$ when $X_H=0.2$ and to $19 \text{ m}^2/\text{g}$ for $X_H=0.6$. Note that this value is comparable with the value of $17 \text{ m}^2/\text{g}$ obtained for the 1st calcination of the limestone. The fundamentals of reactivation by steam hydration clearly rely on the regeneration of part of the microstructure of the original calcined material that, once the Ca(OH)₂ formed during the reactivation process has decomposed, produces an increment in sorbent reaction

surface. As a result, the carbonation conversion of highly reactivated samples is very close to the typical conversion achieved by non-activated samples in their first carbonation cycle. This can be seen, for example, in the conversion curves represented in Figure 3. This Figure represents the CaO conversion curves to CaCO₃ for different number of cycles, corresponding to two experiments that include a reactivation stage every 5 cycles approximately with different level of hydration conversion (X_H , was 0.8 and 0.2 for the experimental data represented in the first row and second row respectively). As it can be observed in Figure 3 a and b), the CaO conversion of the sorbent in cycles 6 and 16, right after its reactivation, is very similar to the conversion achieved by the sorbent in the first cycle. These results corroborate the view that the CO₂ carrying capacity of any CaO-based sorbent (including reactivated samples) is proportional to the internal surface of free CaO for many natural sorbents and typical carbonation and calcination conditions.^{7, 34-36} It has been also observed that reactivation of the sorbent is more effective for particles with moderate activity. For example, in Figure 3 d) low hydration conversion (20% hydration) is able to produce an important increase in CaO conversion to CaCO₃ from 0.30 to 0.40. However, when the same hydration conversion is applied to a more active sorbent (Figure 3 c), the gain in CO₂ capture capacity is moderated (from 0.42 to 0.46 approximately).

Figure 3.

The drastic modifications of pore structures by hydration represented in Figure 2 will also affect the carbonation reaction rate of the sorbent. These conversion curves in Figure 3 are very similar to others described in previous published works on the carbonation reaction. After a fast initial reaction controlled by chemical reaction (kinetic regime) there is an abrupt change in the carbonation reaction rate. This change to a second slower stage has been attributed to the control of CO₂ diffusion via the formation of a CaCO₃ layer that seals off the free surfaces of CaO at the end of the fast reaction period.^{7, 34-38} As it can be seen in Figure 3 a) to d), the carbonation rate of the sorbent has increased in all the cycles that include a reactivation stage with respect to cycles that do not incorporate reactivation. The increments in the slope of the initial fast reaction stage range between 50 to 80%. It is also to be

noted that, although the hydration is moderate for lower values of X_H (as low as 0.2 in Figure 3c and d) hydration still produces an improvement in the reaction rate of the sorbent.

The highest levels of hydration result in large net changes in carrying capacity and reactivity (see Figure 3 a and b). However, it has been reported that these levels of hydration also result in drastic changes in the mechanical properties of the particles.³ In order to quantify these effects, a simple laboratory test was conducted to measure the evolution of the crushing strength of two different batches of reactivated and non-activated particles as described in the experimental section of the paper. The results compiled in Table 1 are expressed in Newtons and represent the average value of the individual crushing strength measured to 20 particles on every stage, and the range in Newtons of deviation in the measures of every sample. From the results, it can be seen that calcined limestone particles are much softer than raw limestone particles and that they break up with the application of a smaller force. It should also be noted that the hydrated particles present a very similar mechanical strength to the calcined particles and that the carbonated particles subjected to reactivation have a lower crushing strength than the non-activated carbonated particles.

Table 1.

Further studies may be needed in this direction to see whether these simple laboratory trends can be confirmed by subjecting the sorbents to attrition tests under more realistic mechanical conditions.

DISCUSSION

As reported in the previous sections, it is clear both from previous works and from experimental results presented in this work that hydration can be an effective technique for reactivating individual particles of CaO with respect to a subsequent carbonation reaction. This is a necessary precondition for implementing a practical reactivation process based on hydration. However, this alone is not sufficient. Several other important factors for the integration of the hydration reactor in the overall system have to be considered. Steam consumption, for example, needs to be minimised for a given improvement in CO₂ capture capacity by means of hydration. High hydration conversions lead to higher reactivation levels,

but also to a higher steam consumption in the hydration reactor. As demonstrated in a previous work,³² the best set-up for incorporating reactivation by hydration should aim at the least possible steam consumption for a given target of average sorbent carrying capacity. This minimum can be achieved via two extreme strategies depending on the level of hydration conversion in the individual particles, X_H : low values of hydration conversion for a large fraction of solids circulating between the calciner and carbonator or, a very high level of hydration for a small fraction of solids circulating between the reactors. In the first case, all the particles experience hydration in each carbonation-calcination cycle, while in the second case, the particles will statistically undergo reactivation only once over several cycles of calcination/carbonation.³² The experimental approach used to analyze the fate of the sorbent in both cases must be different as discussed below, but our analysis of the experimental results will be similar.

Equation (2) has been used as an approach to describe the evolution of sorbent CO_2 carrying capacity, when a hydration stage is included in the system. This equation has a similar structure to Equation (1), and the parameters k_H and X_{rH} will represent the deactivation constant, and the residual molar conversion of the sorbent in a system that includes the reactivation of the sorbent. In this case, k_H and X_{rH} will mainly depend on the reactivation process: this is on the fraction of solids reactivated on every cycle (f_H) and on the conversion achieved by the sorbent in the hydrator (X_H).

$$X_{NH} = \frac{1}{\frac{1}{(1 - X_{rH})} + k_H N} + X_{rH} \quad (2)$$

X_{NH} by this Equation represents the average activity of the sorbent. For a system that includes the reactivation of the whole stream of solids on every cycle ($f_H=1$) X_{NH} represents also the activity of the individual particles but, when only a fraction of solids is reactivated on every cycle ($f_H \neq 1$), X_{NH} will represent the average activity of the whole stream of sorbent.

Moreover, in order to compare series of experiments where particles experience only occasional hydration steps, it is useful to use the cumulative moles of CO_2 absorbed per mol of CaO in N full

carbonation-calcination cycles (Y_N or Y_{NH} when reactivation takes place). Figure 4 a), whose data was originally reported in a previous work³⁹ shows two experimental series that illustrates the effect of different levels of X_H on the carrying capacity of a sorbent, X_{NH} , when a hydration stage is incorporated into every calcination-carbonation cycle. The corresponding k_H and X_{RH} from Equation (2) have been calculated and are compiled in Table 2. The fitting curves have been included in the figure together with the maximum possible capture capacity for each sample without reactivation (calculated according to Equation 1). Figure 4 b) represents the same data obtained by using the cumulative fraction of CO_2 (Y_N , or Y_{NH} for the experiments that include reactivation) absorbed by a sorbent in N full carbonation-calcination cycles. As an example, the highly hydrated sorbent ($X_H=0.6$) can maintain its carrying capacity, X_{NH} , over 0.5 moles of CO_2 captured per mol of CaO and increase by 87% the cumulative fraction of CO_2 transported with respect to the non-reactivated samples after 20 reaction cycles. These improvements tend to increase as the number of cycles increases. This highlights the importance of reactivation by hydration in systems that need to operate with particles that have long life spans (low make up flows of fresh limestone used in the CO_2 capture loop). In contrast, sorbent reactivation by steam hydration would not be attractive in systems working with high sulfur, and ash content fuel, because they would require an important make-up flow of sorbent to control the ash and $CaSO_4$ built up in the system

Figure 4.

These results are in agreement with those reported by Manovic and Anthony¹⁹ who obtained carbonation degrees close to 70% with a highly reactivated sample after ten reaction cycles. Zeman³⁰ reported higher levels of conversions to $CaCO_3$ (up to 0.9) after the first calcination-hydration-carbonation cycle. However, it should be noted that their experiments were carried out with a very fine powdered reagent grade $CaCO_3$ and long carbonation reaction periods. Naturally such conditions would lead to a very high carbonation conversion⁵, although such results give a rather artificial picture as they do not take into account the practical difficulties involved in handling materials as fine as these.

As pointed out before, when the second reactivation strategy is applied (i.e. reactivation of only a fraction of the particles that are circulating between the calciner and carbonator, f_H), the experiments in the laboratory need to be designed to compensate for several cycles without reactivation. Figure 5 shows the results of several experiments in which hydration was applied once every five reaction cycles ($f_H=0.2$). There were exceptions as in Figure 5 c), where the hydration of the sorbent took place every four cycles (between cycles 11th and 15th, and cycles 20th to 24th). The hydration extent of the sample was varied among the experiments as is shown: $X_H=0.8$ in Figure 5 a), $X_H=0.4$ in Figure 5 b), $X_H=0.2$ in Figure 5 c) and finally $X_H=0.1$ in Figure 5 d). As expected, the level of hydration strongly influences the extent of carbonation after reactivation. The best results are obtained when the sample is hydrated up to $X_H=0.8$ and sorbent carbonation capacity can be maintained at close to 0.6. At the opposite extreme, sorbent hydrations of the order of 10% do not offer any important benefit for CO₂ capture capacity because under these conditions the water is only reacting with the CaO that is already active.

Figure 5.

It is also to be noted that the sorbent resulting from hydration tends to decay from its initial gain in carrying capacity faster than natural sorbents. This is clear from the series presented in Figure 5 that exhibits the highest hydration conversion per cycle ($X_H=0.8$ and 0.4). It is therefore evident from these results that the average activity of the materials resulting from these reactivation sequences is lower than one would expect from the increases in activity observed in each cycle, at least for this particular limestone. The experimental data fitted to Equation (2) yield the corresponding k_H and X_{rH} (compiled in Table 2). These experimental data have also been represented in terms of the cumulative CO₂ transported per mol of CaO during the continuous cycling of particles between carbonator and calciner as Y_N and Y_{NH} . In the example marked in Figure 6 a) one mol of CaO after 20 calcination/carbonation cycles is able to transport 5.8 moles of CO₂ per mol of CaO. If this mol of CaO undergoes reactivation after every 5 calcination/carbonation cycles, when 80% of the sample has been hydrated, it will be able to transport around 8.25 moles of CO₂ per mol of CaO.

Figure 6.

Y_N and Y_{NH} have been calculated to a higher number of cycles making use of the parameters k_H and X_{rH} to calculate X_{NH} with the number of cycles. They have been represented in Figure 6 b) to illustrate that the residual conversion of the sorbent (X_r or X_{rH} when reactivated) dominates the cumulative CO_2 absorbed by the sorbent for particles with long lifetimes (high N). This is the most likely scenario for reactivation processes because the reason for using them in the first place is to avoid the need for high make up flows of limestone. This means that the rate of CO_2 captured as $CaCO_3$ (F_{CaCO_3}) in a system that involves a hydration step will be closely represented by:

$$F_{CaCO_3} = F_{CaO} X_{rH} \quad (3)$$

To compare the results obtained from the two reactivation strategies and to determine which is more efficient, we will use as criterion of comparison the rate of steam consumed F_{H_2O} for a given rate of CO_2 captured, F_{CaCO_3} . The steam consumption due to reaction can be calculated as follows:

$$F_{H_2O} = f_H F_{CaO} X_H \quad (4)$$

where F_{CaO} is the stream of solids circulating between calciner and carbonator, f_H the fraction of this stream diverted to the hydration reactor and X_H , the conversion to $Ca(OH)_2$ achieved in this last reactor.

The best scenario for the reactivation process from the point of view of steam consumption would therefore be to minimize the F_{H_2O}/F_{CaCO_3} ratio.

$$\frac{F_{H_2O}}{F_{CaCO_3}} = \frac{f_H X_H}{X_{rH}} \quad (5)$$

If we extrapolate the experimental results presented in this paper to calculate the previous ratio, we find that there are certain important practical limits to reactivation processes by hydration. In the first three columns of Table 2 we include for the two values of f_H (hydration in each cycle as in Figure 4 means $f_H=1$, and hydration every five cycles as in Figure 5 means $f_H=0.2$) the average k_H and X_{rH} of the resulting sorbent (best fit represented by the dotted lines in Figures 4 and 5).

Table 2.

As shown in Figure 6 b), the residual conversion of the sorbent dominates the cumulative CO_2 transported in systems working with low sorbent make-up flow. Therefore, an additional column

showing the ratio between the CO₂ absorbed by the sorbents with and without reactivation, represented by X_{rH}/X_r has been included in Table 2. As expected, the highest improvement in sorbent performance is represented by the highest ratio of X_{rH}/X_r , which is obtained by hydrating the sorbent at every cycle up to $X_H=0.6$. However, as indicated in the last column of Table 2 (F_{H_2O}/F_{CaCO_3}), it has been estimated that this improvement is gained at the expense of a greater consumption of steam in the system, in this case 1.2 mol of steam per mol of CO₂ captured. Clearly, there must be a trade off between the two objectives in the reactivation process: a reasonable high improvement in the CO₂ carrying capacity of the sorbent (high X_{rH}/X_r) and at the same time low steam consumption. There is evidence in Table 2 that this compromise could be best represented by the experimental series in which the sorbent is reactivated every 5 cycles ($f_H = 0.2$) up to a $X_H=0.8$. However, against this choice is the tendency for highly hydrated particles to deteriorate in terms of mechanical properties, as reported in the results section. This illustrates again the need to design a comprehensive sorbent reactivation test that takes into account all of the aspects that affect the process rather than to rely on one controlled laboratory test designed to maximize the increase in activity of individual particles.

CONCLUSIONS

Sorbent reactivation by steam hydration has been proposed as a suitable technique to improve sorbent performance in terms of carrying capacity and carbonation reaction rates. The hydration process can drastically change the pore structure of the carbonating particles by developing a relevant fraction of pore volume with pores ≈ 20 nm that offers much higher CO₂ carrying capacities and carbonation reaction rates. However these textural changes are also responsible for the poorer mechanical properties reflected in the crushing strength test.

In a continuous sorbent reactivation process, solids after hydration should be directed to the carbonator unit and not to the calciner unit because the increase in carrying capacity during hydration is largely lost if this is followed by calcination at temperatures higher than 750°C.

Reactivation of the sorbent by hydration at every cycle has been shown to increase the residual carrying capacity of the sorbent by a factor of 6.6. However, steam consumption in these conditions may be unacceptably high (estimated over 1.2 mol of H₂O per mol of CO₂ captured). A reasonable strategy to moderate steam consumption in the hydration process would be to hydrate only a fraction of the solids circulating between the reactors in the Ca looping cycles, to the maximum level allowed by the constraint imposed by the mechanical strength of the reactivated material. It is also important to highlight that the reactivation by hydration may not be attractive in systems operating with particles that have moderate life spans.

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NOMENCLATURE

f_H = fraction of solids circulating between reactors in the Ca-looping system that undergo to the reactivation process

F_{CaO} = molar flow of CaO circulating in the Ca-looping system between calciner and carbonator

F_{CaCO_3} = CO₂ capture rate, expressed as molar flow of CaCO₃ formed in the carbonator

F_{H_2O} = molar flow of steam reacting with CaO in the hydration reactor

k = sorbent deactivation constant, Eq. 1

k_H = sorbent deactivation constant in a system that includes a reactivation stage, Eq. 2

X_H = CaO molar conversion to Ca(OH)₂ during the reactivation by steam hydration

X_N = CaO molar conversion to CaCO₃ at cycle N

X_{NH} = average CaO molar conversion to CaCO₃ at cycle N, for a system that includes reactivation

X_r = sorbent molar conversion to CaCO₃ after an infinite number of cycles

X_{rH} = sorbent molar conversion to CaCO₃ after an infinite number of cycles in a system that includes reactivation

Y_N = cumulative moles of CO₂ transported per mol of CaO after N full calcinations/carbonation cycles

Y_{NH} = cumulative moles of CO₂ transported per mol of CaO after N full calcinations/carbonation cycles in a system that includes reactivation of the sorbent

REFERENCES

- (1) Harrison, D.P. *Ind. Eng. Chem. Res.* **2008**, 47, 6486-6501.
- (2) Anthony, E.J. *Ind. Eng. Chem. Res.* **2008**, 47, 1747-1754.
- (3) Blamey, J.; Anthony, E.J.; Wang, J.; Fennell, P.S. *Progr. Ener. Comb. Sci.* ,**2010**, 36, 260-279.
- (4) Curran, G. P.; Fink, C. E.; Gorin, E. *Adv. Chem. Serv.* **1967**, 69,141-65.
- (5) Barker, R. *J. Appl. Chem. Bio.* **1973**, 23, 733-742.
- (6) Abanades, J.C. *Chem. Eng. J.* **2002**, 90, 303-306.
- (7) Abanades, J.C.; Alvarez, D. *Energy Fuels* **2003**, 17, 308-315.
- (8) Wang, J.; Anthony, E.J. *Ind. Eng. Chem. Res.* **2005**, 44, 627-629.
- (9) Grasa, G.S.; Abanades, J.C. *Ind. Eng. Chem. Res.* **2006**, 45, 8846-8851.
- (10) Lysikov, A.I.; Salanov, A.N.; Okunev, A.G. *Ind. Eng. Chem. Res.* **2007**, 46, 4633-4638.
- (11) Li, Z.; Cai, N. *Energy Fuels* **2007**, 21, 2909-2918.
- (12) Alonso, M.; Rodríguez, N.; González, B.; Grasa, G.; Murillo, R.; Abanades, J.C. *Int. J. Greenhouse Gas Control Tech.* **2010**, 167-173.
- (13) Charitos, A.; Hawthorne, C.; Bidwe, A.R. et al. *Powder Tech.* **2010**, 200(3) 117-127.
- (14) Rodríguez, N.; Alonso, M. and Abanades, J.C. *AIChE J.* doi:10.1002/aic.12337.
- (15) Rodríguez, N.; Alonso, M.; Grasa, G.; Abanades, J.C. *Chem. Eng. J.* **2008**, 138, 148-154.
- (16) Martínez, I.; Murillo, R.; Grasa, G.; Abanades J. C. *AIChE J.* 10.1002/aic.12461.

- (17) Lisbona, P.; Martínez, A.; Lara, Y.; Romeo, L.M. *Energy Fuels* **2010**, 24, 728-736.
- (18) Hughes, R.W.; Lu, D.; Anthony, E.J.; Wu, Y. *Ind. Eng. Chem. Res.*, **2004**, 43, 5529-5539.
- (19) Manovic V., Anthony E.J. *Env. Sci. Tech.* **2007**, 41, 1420-1425.
- (20) Manovic V., Anthony E.J. *Fuel* **2008**, 87(8-9), 1564-1573.
- (21) Manovic, V.; Anthony, E.J. *Thermal Sci.* **2009**, 13(1), 89-104.
- (22) Fennell, P.S.; Davidson, J.F.; Dennis, J.S.; Hayhurst, A.N. *J. Energy Inst.* **2007**, 80(2), 116-119.
- (23) Manovic V., Anthony E.J., Lu D.Y. *Fuel* **2008**, 87, 2923-2931.
- (24) Manovic V.; Lu, D.; Anthony E.J. *Fuel* **2008**, 87, 3344-3352.
- (25) Sun, P.; Grace, J.R.; Lim, J.C.; Anthony E.J. *Ind. Eng. Chem. Res.* **2008**, 47, 2024-2032.
- (26) Wu Y., Blamey J., Anthony E.J., Fennell, P.S. *Energy Fuels* **2010**, 24, 2768-2776.
- (27) Curran G.P. Patent U.S. N° 3, **1970**, 516, 808.
- (28) Anthony, E.J.; Bulewicz, E.M.; Jia, L. *Prog. Energy Combust Sci.* **2007**, 33, 171-210.
- (29) Laursen, K.; Duo, W.; Grace, J.R.; Lim, J. *Fuel* **2001**, 80, 1293-1306.
- (30) Zeman F. *Int. J. of Greenhouse Gas Control* **2008**, 2, 203-209.
- (31) Zsako J., Hints M. 1998. *J. Therm. Anal.* **1998**, 53 323-331.
- (32) Arias, B.; Grasa, G.S.; Abanades, J.C. *Chem. Eng. J.* **2010**, 163, 324-330.
- (33) Brunauer, S.; Emmett P.H. and Teller J. *J. Amer. Chem. Soc.* **1938**, 60, 309-319.
- (34) Alvarez, D.; Abanades, J.C. *Ind. Eng. Chem. Res.* **2005**, 44, 5608-5615.
- (35) Alvarez, D.; Abanades, J.C. *Energy Fuels* **2005**, 19, 270-278.

(36) Sun P.; Grace J.R.; Lim C.J.; Anthony, E.J. *Chem. Eng. Sci.* **2008**, 63, 57-70.

(37) Bathia, S. K.; Perlmutter, D.D. *AIChE J.* **1983**, 39, 79-86.

(38) Grasa, G.; Murillo, R.; Alonso, M.; Abanades, J.C. *AIChE J.* **2009**, 55 (5), 1246-1255.

(39) Grasa, G.; Murillo, R.; Alonso, M.; González, B.; Rodríguez, N.; Abanades, J.C. 4th International Conference on Clean Coal Technologies, Dresden, Germany, **2009**.

FIGURES

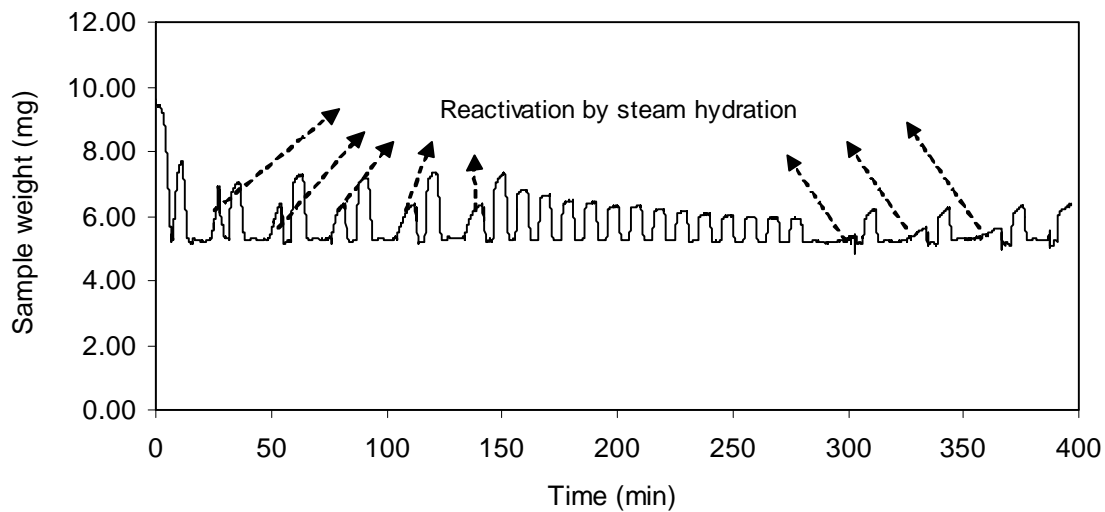


Figure 1. Experimental data expressed as weight vs. time for the calcination-hydration-carbonation cycles.

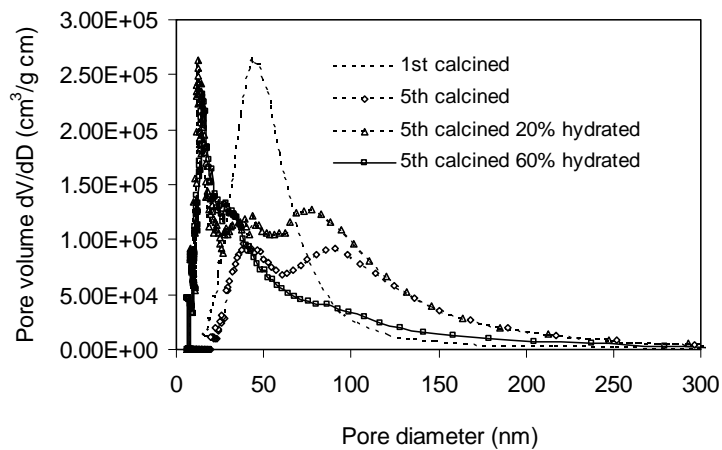


Figure 2. Pore-size distribution of the different samples tested. Samples: 1st calcined sample obtained from the first calcination of limestone; 5th calcined sample obtained after 5 reaction cycles; 5th calcined 20% hydrated sample obtained after hydration up to 0.2 molar conversion of the 5th calcined sample; 5th calcined 60% hydrated sample obtained after hydration up to 0.6 molar conversion of 5th calcined sample.

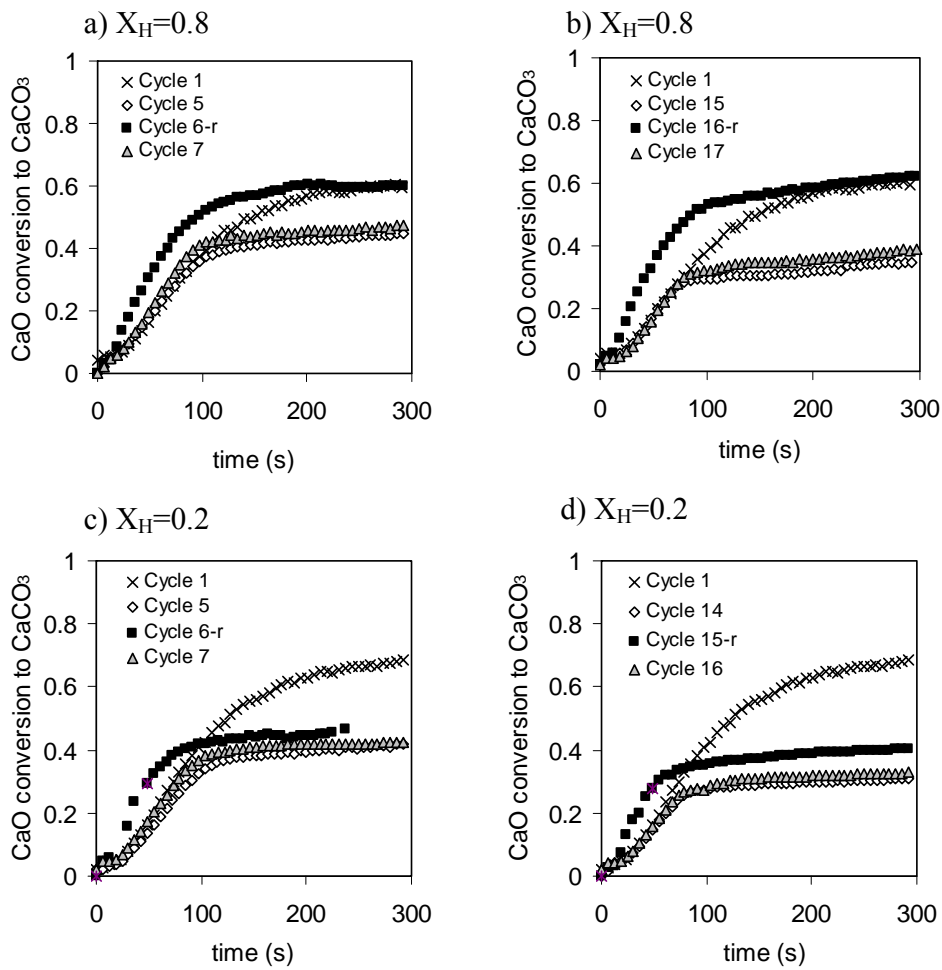


Figure 3. CaO to CaCO₃ conversion curves vs. time for different number of cycles from two experiments that include the reactivation of the sorbent. Figures a and b): reactivation in cycle 6 and 16, up to 80% hydration molar conversion ($X_H=0.8$). Figures c and d): reactivation in cycle 6 and 15, up to 20% hydration molar conversion ($X_H=0.2$).

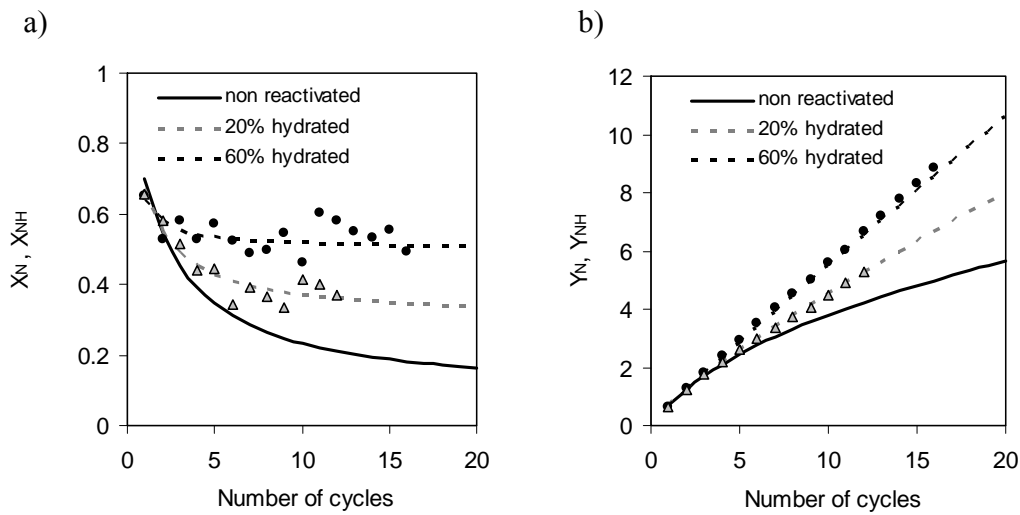


Figure 4. a) CaO molar conversion to CaCO₃ vs. number of cycles for experiments including a reactivation stage on every cycle up to $X_H=0.2$ and 0.6 respectively. b) Cumulative CO₂ transported per mol of CaO for reactivated samples and for a non-reactivated sample (solid line).

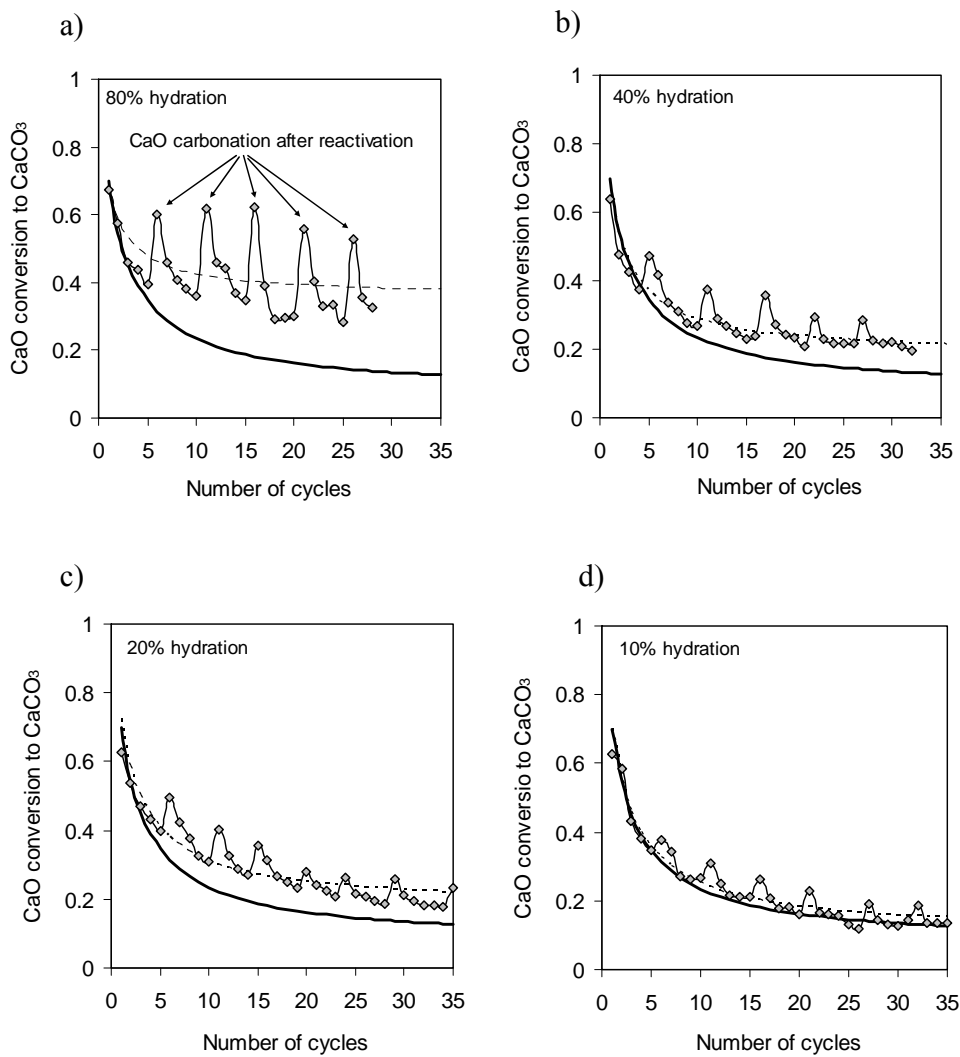


Figure 5. CaO molar conversion to CaCO₃ vs. number of cycles for samples reactivated once every 5 cycles. a) X_H=0.8; b) X_H=0.4; c) X_H=0.2; d) X_H=0.1. Solid lines represent X_N obtained from Eq. 1, dotted lines represent X_{NH} obtained from Eq. 2. Measured data are represented by symbols.

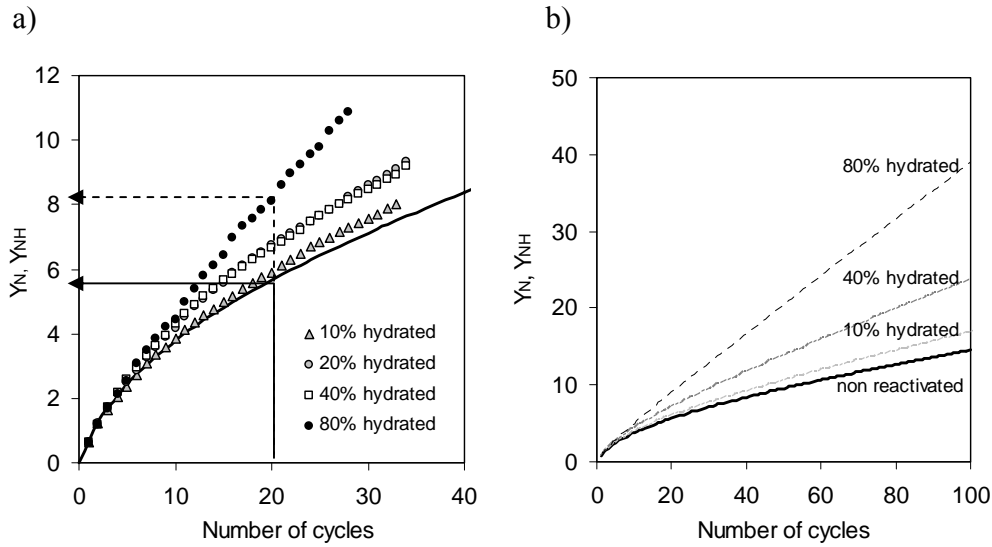


Figure 6. a) Cumulative moles of CO₂ transported per mol of CaO for reactivated and non-reactivated samples (solid line). b) Cumulative moles of CO₂ transported per mol of CaO extrapolated to a higher number of cycles.

TABLES

Table 1. Crushing strength measured to a non-reactivated calcined/carbonated sample and to a calcined/reactivated/carbonated sample.

Non reactivated sample	Crushing strength (N)
Raw limestone	8.05 ± 1.5
1 st calcination	2.86±1.0
1 st carbonation	7.54±1.7
Reactivated sample	Crushing strength (N)
Raw limestone	8.05±1.5
1 st calcination	2.86±1.0

Hydration ($X_H=0.8$)	3.4 ± 1.0
1 st carbonation	5.35 ± 1.7

Table 2. Steam consumption and improvements in CO₂ capture for the different hydration strategies adopted in this work. The Table also includes the values of the deactivation constant and residual activity obtained through fitting of the experimental work presented.

f_H	X_H	k_H	X_{rH}	X_{rH}/X_r	F_{H_2O}/F_{CaCO_3}
1	0.6	5.26	0.5	6.6	1.20
1	0.2	1.26	0.29	3.8	0.68
0.2	0.8	1.38	0.36	4.8	0.44
0.2	0.4	0.81	0.18	2.4	0.44
0.2	0.2	0.61	0.17	2.4	0.22
0.2	0.1	0.55	0.1	1.3	0.20