A model for self-reactivation of highly sintered CaO particles during CO₂ capture looping cycles

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ABSTRACT. Calcium looping is an emerging high-temperature, energy-efficient, CO₂ capture technology using CaO as a regenerable sorbent of CO₂ through the reversible carbonation/calcination reaction. The stability of the sorbent plays a key role in the design of these systems. This paper revisits the self-reactivation phenomenon that has been reported for some highly deactivated CaO materials when submitted to repeated carbonation/calcination cycles under certain conditions. Self-reactivation is modelled in this paper as the result of a dynamic balance between the loss of activity in one cycle and the accumulated gain of activity by extended carbonation times, due to a product layer of CaCO₃ that keeps building up on all surfaces, controlled by the slow diffusion of CO₂. The model describes reasonably well the trends observed for some limestones and conditions. For other limestones and conditions, the carbonation mechanism is more complex and the model does not fit the evolution of the maximum Ca conversion with the number of cycles as well, although the general patterns of self-reactivation are still well reproduced.

KEYWORDS Ca-looping, CO₂ capture, self-reactivation.

INTRODUCTION

A range of CaO-based solid looping systems are being proposed for lower cost and higher energy efficiency CO₂ capture from flue gases and syngas¹⁻⁴. These processes are based on the carbonation/calcination equilibrium between CO₂, CaO and CaCO₃. The processes have two main reaction steps: absorption of CO₂ at high temperatures using the carbonation reaction of CaO and desorption of highly concentrated CO₂ by oxy-fuel combustion-calcination (or other means to supply the necessary heat for calcination).

Like any other sorption-desorption CO₂ capture system, Ca-looping systems tend to operate with small make-up flow of sorbent and this forces the process to operate with a majority of highly cycled (highly deactivated) particles circulating in the system. One of the main concerns for developers of Ca-looping technologies is that carbonation is fast only for a limited range of conversion and its attainable level falls with the number of cycles. High make-up flows of cheap limestone are economically feasible⁵ under some circumstances. But in order to minimize the requirements of fresh limestone make up, Ca-looping systems are forced to operate with carrying capacities close to the so called residual activity of the material (of around 0.07-0.1)⁶. Recent experimental work aimed at the demonstration of carbonation reactors in continuous postcombustion Ca-looping systems⁷⁻⁹ have shown that the system can yield high capture efficiencies when the low carrying capacities of the sorbent are compensated with sufficiently high solid circulation rates (still reasonable for circulating fluidized bed operation). However, it is clear from these studies that even modest improvements (a few conversion points) in the maximum carrying capacity of the deactivated materials can have a large positive impact on the performance of the reactor (reducing circulation requirements and energy requirements in the calciner). Much effort has been devoted to overcoming the sorbent activity decay by designing new synthetic CaO sorbents, reactivation, preactivation or thermal pretreatment of CaO particles derived from calcination of natural limestones^{1,3,10}. This paper concerns itself only with the last method, also called “self-reactivation”¹¹ that tends to enhance the carrying capacity of the sorbent by submitting it to a precalcination step followed by multiple carbonation/calcination cycles where the sorbent seems to gain capture capacity and maintain a residual activity substantially higher than the original.

Early tests¹², searching for an optimum set of pre-sintering calcination conditions (temperatures and times of calcination higher than normal), leading to improved performance in later carbonation/calcination cycles, failed to deliver any positive results. However, other authors demonstrated that the thermal pretreatment of some limestones at high temperatures showed beneficial effects under some conditions¹³⁻¹⁶ and increases in sorbent carrying capacity with increasing number of reaction cycles were reported. One experimental study¹¹ showed that conversions of four Canadian limestones, after grinding and pre-treatment at temperatures of 1000-1200°C, increased with the number of cycles, reaching ~50% in the 30th cycle. Moreover, work by Chen et al.¹³ demonstrated that the beneficial effect of self reactivation could contribute to enhanced CO₂ capture for over a 1000 cycles. Interestingly, high levels of Na were found to prevent any self reactivation behavior both with natural and doped samples¹⁵. This research also showed that activity could be recovered by grinding the sorbent with Al₂O₃ and it was suggested that the presence of Al in natural limestone might contribute to this effect. What was lacking in this early work was a convincing explanation for these effects other than of the existence of a hard “skeleton”¹⁶, which allowed recovery of activity over repeated calcination and carbonation cycles.

The number of variables involved in the self-reactivation process is large and it is difficult to understand and quantify the underlying carbonation reaction mechanism. The purpose of this work is to advance in this direction by attempting a quantitative explanation of the self-reactivation phenomenon, using the current understanding of the dominant deactivation mechanism of CaO in these systems as the number of carbonation/calcination cycles increases.

CARBONATION REACTION MECHANISM ON HIGHLY SINTERED CAO PARTICLES

The texture of highly sintered particles of CaO after many cycles of carbonation and calcination has been well studied in the literature. The simplest possible model, which holds for different conditions and materials¹⁷, has been outlined in early works by Curran *et al.*¹⁸ and Barker¹⁹. This model assumes an open network of very large pores or inter grain spaces, on average several hundred microns wide. These pores or voids can only be partially filled up by carbonate because there is a certain thickness of the

CaCO₃ product above which reaction rates are low, controlled by diffusion through the layer. Other more complex pore distributions and textural effects may appear under some conditions, but a discussion of these is beyond the objective of this work.

For the open-pore networks characteristic of deactivated CaO particles, derived from multicycle tests or from single pretreatment steps (in self-reactivation experiments), we assume that the basic carbonation model outlined in the previous paragraph is still useful to describe the main features of the carbonation process. In contrast with what happens in other gas solid reactions (like sulphation of CaO), the pore blockage mechanism is not usually responsible for the limited conversion of the CaO with CO₂ after several cycles of carbonation and calcination. In the carbonation reaction, it is the diffusion of CO₂ through the built up layer of calcium carbonate that limits the progress in sorbent conversion. When the product layer covers the free internal surface of CaO to a critical thickness of about 30-50 nm, the fast carbonation period ceases (in less than one minute at typical flue gas conditions and 650°C at atmospheric pressure)²⁰. However, the reaction can still progress at a much slower rate controlled by diffusion (see Figure 1).

Figure 1.

Assuming large enough pores to make the pore size change with conversion negligible and an even distribution of CaCO₃ on the internal surface of CaO, the carbonation conversion of particles in the slow reaction regime should be proportional to the free surface (S_N) and the thickness of the formed layer (h).

$$X_N = S_N \frac{h M_{CaO}}{\rho_{CaO} V_{M_{CaCO_3}}} \quad (1)$$

where M_{CaO} is the molar mass of CaO, ρ_{CaO} is the density of CaO and V_{M_{CaCO₃}} is the molar volume of CaCO₃. This is of course as long as the network of pores can accommodate the layer of product despite the different molar volumes of CaO and CaCO₃ (16.9 and 36.9 cm³/mol respectively). We argue that this is always the case for highly sintered particles (maximum carrying capacities below 0.2) except in extremely long carbonation times (days of reaction, as shown by ^{19, 21, 22}) that are not relevant to this

discussions. On the other hand, it is clear from the very definition of X_N in Eq. 1 and Figure 1 that the conversion achieved in cycle N is the sum of two terms:

$$X_N = X_{KN} + X_{DN} \quad (2)$$

Therefore, for extended carbonation times, there is a critical thickness of the product layer that marks the onset of the slow reaction regime, and that keeps getting thicker with time as the reaction slowly progresses under the diffusion-controlled regime. It is important to highlight here that the deactivation curves of sorbents (plots of the sorbent carrying capacity *vs.* cycle number) that are obtained in laboratory tests to characterize different sorbents, are by definition connected only to the conversion (and product layer thickness) associated with the fast carbonation period. In this work, we have used the equation proposed by Grasa and Abanades⁶:

$$X_{KN} = \frac{1}{\frac{1}{(1 - X_r)} + k N} + X_r \quad (3)$$

where k is the deactivation constant, and X_r is the residual conversion after an infinite number of cycles. These parameters are intrinsic to each sorbent, and depend on the rate of sintering of the particles from an initial state of maximum activity or carrying capacity. Furthermore the proportionality between carbonation conversion and internal surface (S_{KN}) area implies that for highly sintered particles, we can describe the evolution of S_{KN} combining Eq. 1 and Eq. 3. Therefore, for large N (say, higher than 20):

$$S_{KN} = \frac{\rho_{CaO} V_{CaCO_3}}{h M_{CaO}} \left(\frac{1}{\frac{1}{(1 - X_r)} + k N} + X_r \right) \quad (4)$$

Since Eq. 1 and Figure 1 state that the gain of activity under the slow diffusion-controlled regime in each carbonation cycle is also proportional to the surface available for reaction, the carbonation conversion in each cycle (X_N) can be calculated using the following equation:

$$X_N = \left(\frac{1}{\frac{1}{(1 - X_r)} + k N} + X_r \right) (1 + k_D) \quad (5)$$

where k_D is the proportional constant. This new parameter k_D is trying to capture that the small additional conversion, X_{DN} , gained in each cycle after the fast reaction regime is finished, is still proportional (like X_{KN}) to the initial surface area of large voids and the final product layer thickness. Indeed, this equation may have a more general application, since we have recently shown²³, using a detailed pore reaction model²⁰, that the parameters k , X_r and k_D are applicable to fit the slow carbonation process well in series of data obtained with long carbonation times, published by Barker¹⁹ and Lysikov *et al.*¹⁶.

For the purpose of this work, we will use Eq. 5 as the general equation that fits the decay of the sorbent carrying capacity with the number of cycles in experiments that allow a certain period of small additional gains of conversion in each cycle, through extended carbonation. This will be shown to be useful to interpret results published reporting the self-reactivation phenomenon.

QUANTITATIVE ANALYSIS OF SELF-REACTIVATION CURVES

During the thermal pretreatment of the sorbent for self-reactivation test, its activity is reduced due to the sintering of the CaO. There is a drastic drop in internal surface area and associated increase in pore size. As a result, this sorbent will have, after just one calcination, a low initial value of conversion and associated surface area S_N , that is characteristic of highly cycled samples (high N in Eq. 3). This number

of cycles representing the actual “age” of the sorbent, N_{age} , has been defined in previous work²³⁻²⁶ as the effective number of cycles associated with a particle with a given conversion X_N . From equation 3:

$$N_{age} = \left(\frac{1}{k} \right) \left(\frac{1}{X - X_r} - \frac{1}{1 - X_r} \right) \quad (6)$$

If a pre-treated sorbent (with low carrying capacity, X , and high value of N_{age}) is submitted to a carbonation/calcination cycle and the experimental conditions during carbonation allow for the sorbent to react beyond the fast reaction regime, the sorbent will be slightly reactivated during this single carbonation (because it will gain, at the end of the slow carbonation stage, a slightly lower value of N_{age} according to Eq.6). The gain of activity due to carbonation under the diffusion-controlled regime (X_{DN}) can be calculated using the following equation (from Eqs. 3 and 5):

$$X_{DN} = \left(\frac{1}{\frac{1}{(1 - X_r)} + k N} + X_r \right) k_D \quad (7)$$

The small gain in carrying capacity in each cycle associated with the slow carbonation estimated using the previous equation can now be compared, for the same cycle, with the loss in conversion associated with the inherent decay of carrying capacity after each calcination. This loss in carrying capacity can be estimated using the following expression derived from Eq. 3:

$$\Delta X_N = X_{N-1} - X_N = \frac{1}{\frac{1}{1 - X_r} + k(N-1)} - \frac{1}{\frac{1}{1 - X_r} + k N} \quad (8)$$

The balance of sorbent deactivation, ΔX_N , and gain of activity due to carbonation under the diffusion-controlled regime (X_{DN}) in each cycle will determine the carrying capacity of the particles in the next one and thus the evolution of X_N with the number of cycles. The different evolution of both effects with N makes that both terms becomes equal after a certain number of cycles (from which $\Delta X_N = X_{DN}$). From this point, the carrying capacity of the sorbent remains stable with the number of cycles, showing a nearly constant apparent residual activity ($X_{r \text{ apparent}}$). This sort of dynamic equilibrium was also outlined by Chen *et al.*¹³ to explain the gains in sorbent carrying capacity during their self-reactivation experiments. The final shape of the sorbent deactivation curve will depend on the value of k_D .

In order to analyze this dependency we compare (Figure 2) the evolution of sorbent carrying capacity with the number of cycles and the apparent residual conversion observed ($X_{r \text{ apparent}}$) for different values of k_D . We have assumed that the starting material is a sorbent previously deactivated, with a $X_{KN} = 0.20$ in the first cycle, and values of $k = 0.52$ and $X_r = 0.075$ ⁶. For this pre-treated sorbent, we have calculated the evolution of the conversion with the number of cycles (X_N) for different values of k_D up to 0.20. Results in an earlier paper²³ have shown that this parameter can reach values up to 0.25 for intense carbonation conditions (*i.e.*, 24 h of carbonation time, in data from Barker¹⁹), and the fitting of self-reactivation data discussed below will also provide this range of values. If the sorbent reacts only until its maximum conversion under the fast reaction regime ($k_D = 0$), the conversion decays slowly with the number of cycles, towards its intrinsic residual conversion ($X_r = 0.075$). For the example of a value of $k_D = 0.02$, the sorbent has a similar trend because the reactivation in each cycle (X_{DN}) is smaller than the drop in carrying capacity after the completion of the cycle (ΔX_N in Eq. 7). However, the observed carrying capacity with this k_D is already higher compared with the series for $k_D = 0$, and it stabilizes in a few cycles at a value of $X_{r \text{ apparent}}$ around 0.16.

Figure 2.

If k_D is 0.04, the activity of the sorbent remains almost constant with the number of cycles ($X_{r \text{ apparent}} = 0.2$), as the gain of activity is equal to the loss of activity for the first cycle. However, for higher values,

it can be seen that the conversion increases with the number of cycles and it stabilizes at a value higher than the initial conversion ($X_{N=1}$).

This shows that, depending on the carbonation conditions, the sorbent can exhibit self-reactivation, increasing activity with the number of cycles and keep high residual carrying capacities for high numbers of cycles. This semi-empirical exercise also shows the influence of carbonation conditions on the apparent residual activity of the sorbent ($X_{r \text{ apparent}}$). This residual carrying capacity is achieved during cycling when $\Delta X_N = X_{DN}$ as mentioned above. To obtain a quantitative solution for $X_{r \text{ apparent}}$ Eq. 9 can be solved for N:

$$\frac{1}{\frac{1}{1-X_r} + K(N-1)} - \frac{1}{\frac{1}{1-X_r} + K N} = \left(\frac{1}{\frac{1}{1-X_r} + K N} \right) k_D \quad (9)$$

The N obtained as solution of the above equation has to be combined with Eq. 5 into an equivalent value of conversion, X_N , which is equal under these conditions to the apparent residual carrying capacity, $X_{r \text{ apparent}}$. It should be noted that the equilibrium value of $X_{r \text{ apparent}}$ is dependent only on the value of k_D for the sorbent (with intrinsic values of X_r and k), and it is independent of the initial activity of the sorbent. This is shown in Figure 3, where the evolution of the carrying capacity is plotted for different starting activities ($X_{N=1}$) and for a constant value of $k_D = 0.10$ (using $X_r = 0.075$ and $k = 0.52$). As can be seen in this figure, the self-reactivation is only observed when the starting activity of the material $X_{N=1}$ is lower than $X_{r \text{ apparent}}$. Under these conditions, there is an apparent increase of X_N as the number of cycles increases. However, if $X_{N=1} > X_{r \text{ apparent}}$, the self-reactivation of the sorbent will not be observed.

Figure 3.

The results of Figure 3 indicate that if the model proposed in this work is correct, no benefit can be obtained from pre-sintering or pre-calcining the sorbent, because under identical carbonation conditions, the carrying capacity of the sorbent would converge to the same apparent residual activity.

In order to validate the discussion carried out in the previous paragraphs we have used the results published by Manovic and Anthony¹¹. The data correspond to four sorbents that were derived from natural limestones, after being powdered ($< 50 \mu\text{m}$) and pre-treated at 1000°C during 6 h in nitrogen. After this pretreatment, the sorbents were submitted to 30 carbonation/calcination cycles at 800°C . Carbonation was carried out for 30 min using a $p\text{CO}_2 = 0.5 \text{ atm}$, and calcination for 10 min in pure N_2 .

As can be seen in Figure 4, some differences are observed in the initial carrying capacity of the sorbent. However, during cycling the evolution of their XN values is qualitatively similar, increasing with N towards an almost constant level, different for each sorbent and substantially higher than expected value of residual activity (self-reactivation effect). The values of $X_{r \text{ apparent}}$ are included in Table 1.

Figure 4.

Using the experimental data compiled in Figure 4, we have fitted the data to Eq. 5 and estimated the value of k_D using values of $k = 0.52$ and $X_r = 0.075^6$. The comparison between experimental and calculated values can be seen in Figure 4. As can be observed, there is reasonable agreement between experimental and calculated conversions. The main discrepancies are observed in the case of samples from the GR limestone, probably due to low conversion achieved during the initial cycles. However, in all cases, it can be seen that the methodology proposed can describe the self-reactivation, showing that the sorbent conversion can increase with the number of cycles.

Table 1 summarizes the calculated values of k_D . Similar values of k_D were obtained for the different limestone samples. This result was as expected as the sorbents have been tested under the same experimental conditions. The high values of k_D obtained show that carbonation conditions used allow a substantial progress in the carbonation conversion in each cycle under the diffusion-controlled regime, which explains the gain of activity with the number of cycles (see Fig. 4).

Table 1.

In the paper presented by Manovic and Anthony¹¹ and in a later published work¹⁴ the authors reported a different behavior of self-reactivation for coarser particles ($> 300 \mu\text{m}$). In this case, sorbent

conversion increased with the number of cycles until it reached a maximum at a low number of cycles (lower than $N=15$), from which it decreased slowly until an almost constant value was achieved. The maximum observed cannot be explained by arguing sorbent reactivation only by extended carbonation. In this case, other effects have to influence the evolution of the carrying capacity of the sorbent during cycles. A possible explanation of this behavior may be based on a heterogeneous sintering of the particles during thermal pretreatment. This could lead to a deeper deactivation of the external shell of the particles, leaving some active CaO in the particle core. In this case, the reactivation by carbonation in each cycle could gradually destroy the external sintered sorbent, which would expose active sorbent in the next cycle. As a result, the activity of the particle could then increase until the disappearance of the sintered layer. Then it would present a “typical” decay of carrying capacity during cycling down to the residual conversion, determined by carbonation conditions. Other experimental results about self-reactivation presented by Chen *et al.*¹³ have shown that thermal pretreatment of a natural limestone can modify the residual conversion of the sorbent after a thousand calcination/carbonation cycles, indicating that some sorbents can deviate from the general trends shown in this work.

Recently Manovic and Anthony²⁷ reported that under certain conditions, the surface of sorbent particles is more liable to sintering; in this case an external layer of carbonate can be formed, preventing CO₂ diffusion to the inner core of the particles. On the other hand, other authors¹² have reported that certain carbonation conditions can lead to the formation of narrow bottlenecks that may limit sorbent conversion. These studies have shown that complex CaO arrangements can occur which may lead to uncommon behavior.

A final point for discussion is on the implications of the analysis carried out in this work to assess the practical viability of self-reactivation strategies in Ca-looping systems. For postcombustion systems operating with circulating fluidized bed carbonators, the short residence times of particles in the carbonator, operating at low partial pressures of CO₂, will make an effective self-reactivation of the sorbent impossible (the value of k_D will be very close to 0, as the particles will react mainly under the fast reaction stage). The carrying capacity of the particles will decrease with the number of cycles

towards a low value of residual activity (X_r). In contrast, in precombustion Ca-looping routes (e.g., gasification), the carbonation conditions are likely to be more intense (higher partial pressure of CO_2 and/or contact times between CaO particles and a CO_2 -rich gas). This may lead to strong self-reactivation phenomena, with sorbent carrying capacities moving towards higher apparent residual activities.

CONCLUSIONS

The phenomenon of self-reactivation can be explained taking into account that carbonation conditions can induce a certain reactivation of the particles in each cycle if the sorbent is allowed to react under the diffusion controlled regime. Depending on the carbonation conditions and the starting activity of the sorbent before cycling, the carrying capacity can be increased with the number of cycles if the gain of activity induced by prolonged carbonation is higher than the deactivation due to calcination. The methodology used in this work, based on sorbent reactivation due to prolonged carbonation, is able to describe the self-reactivation of pulverized thermal pretreated sorbents. Coarser particles present a different behavior and a maximum occurs in the curve representing the evolution of the carrying capacity with the number of cycles. In this case, more factors are influencing the performance of the sorbent during cycling.

Self-reactivation may not be expected under typical reaction conditions of a CFB carbonator where the reaction time will be limited to a few minutes at CO_2 partial pressures below 10 kPa and temperatures around 650°C.

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NOTATION

h	product layer thickness, m
k	sorbent deactivation constant

k_D	proportional constant
M_{CaO}	molecular weight of CaO, kg/kmol
N	number of calcination/carbonation cycles
S_{KN}	reaction surface, m^2/m^3
VM_{CaCO_3}	molar volume of $CaCO_3$, $m^3/kmol$
X_{DN}	CaO molar conversion under the diffusion-controlled regime
X_{KN}	CaO molar conversion under the fast-reaction regime
X_N	CaO molar conversion in each cycle
X_r	residual CaO conversion
k_D	proportional constant in Eq. 5
ΔX_N	Loss in carrying capacity
ρ_{CaO}	CaO density, kg/m^3

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FIGURES

Figure 1. Schematic representation of sorbent conversion during the slow part of the carbonation reaction.

Figure 2. Evolution of sorbent carrying capacity with the number of cycles with a starting carrying capacity of $X_{KNI} = 0.2$ for different values of k_D (0.00, 0.02, 0.04, 0.10 and 0.15) using values of $k = 0.52$, $X_r = 0.075$.

Figure 3. Evolution of sorbent carrying capacity with the number of cycles for different starting sorbent activities ($k_D = 0.10$, $k = 0.52$, $X_r = 0.075$).

Figure 4. Comparison of experimental carbonation conversion (dots) with calculated values using Eq. 5 (continuous lines) for pre-treated limestones KR, HV, CD and GR (experimental data from¹⁰).

TABLES

Table 1. Calculated values of k_D using the experimental data presented in Figure 4.

Limestone	KR	HV	CD	GR
k_D	0.16	0.17	0.13	0.18
$X_{r \text{ apparent}}$	0.46	0.47	0.38	0.50