Sorbent attrition in a carbonation/calcination pilot plant for capturing CO₂ from flue gases

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Abstract

There is increasing interest in CO₂ looping cycles that involve the repeated calcination and carbonation of the sorbent as a way to capture CO₂ from flue gases during the carbonation step and the generation of a pure stream of CO₂ in the oxyfired calcination step. In particular, attrition of the material in these interconnected fluidized bed reactors is a problem of general concern. Attrition of limestone derived materials has been studied in fluidized-bed systems by numerous authors. In this work, we have investigated the attrition of two limestones used in a system of two interconnected circulating fluidized bed reactors operating in continuous mode as carbonation and calciner reactors. We observed a rapid initial attrition of both limestones during the calcination step which was then followed by a highly stable period (up to 140 h of added circulation for one of the limestones) during which particle size changes were negligible. This is consistent with previous observations of attrition in other systems that employ these materials. However, a comparison of the attrition model constants with the data reported in the literature showed the two limestones to be particularly fragile during the initial calcination and the first few hours of circulation. Thus, a careful choice of limestone based on its attrition properties must be taken into account in designing future carbonate looping systems.

Keywords: CO₂ capture, limestone, attrition, fluidized bed

1. Introduction

There are many possible approaches for capturing CO₂ [1]. We have focussed in this paper on the separation of CO₂ from a flue gas stream using regenerable solid sorbents based on the CaO/CaCO₃ carbonation/calcination loop [2]. The basic scheme of the process is depicted in Figure 1. This system consists of two interconnected circulating fluidized bed reactors: a carbonator and a calciner. In the carbonator, the CO₂ present in the combustion flue gas reacts with the CaO to form CaCO₃. The solids leaving the carbonator are then directed to the calciner where calcination/regeneration takes place, while a stream of depleted CO₂ gas leaves the carbonator. In this second reactor, the CaCO₃ formed in the carbonator is calcined and decomposes into CaO (which then returns to the carbonator) and CO₂, which is now suitable for final purification, compression, and geological storage. Calcination is usually carried out by oxyfuel combustion. Combustion-based systems of this type are described in more detail elsewhere [2, 3].

The inherent advantages of the system of Figure 1 are now widely recognised and many fundamental problems have been solved [2]. There is now a growing interest in reporting the attrition behaviour of the materials in the circulating calcination-carbonation loops [4]. Although information on attrition in systems such as that in Figure 1 is scarce, background information on attrition in fluidized-bed combustors is abundant [4-22]. It has long been known that for fluidized bed combustion systems [7], particles from the fuel (coal, char, ash etc) or the SO₂ sorbent (limestone, dolomite, etc) are attrited by the mechanical forces in the bed, while chemical reactions are taking place. The direct consequence of this phenomenon is that the number of particles increases as the particle size of the remaining solids decreases.

In order to study the attrition characteristics of limestones, several authors have proposed different tests for these solids' [13, 17, 18, 19, 23, and 24]. A detailed simulation of attrition requires a fundamental study of the mechanical characteristics of the materials and a thorough understanding of the breaking energy supplied by the system to the individual particles. However, for highly heterogeneous fluidized bed systems, like combustors, this is not a reasonable modelling approach, and more empirically orientated attrition models have been proposed. Chirone et al.[21] suggested that the reduction in the size of the particles was probably the result of four mechanisms: abrasive attrition, primary and secondary fragmentation, and fragmentation by uniform percolation, occurring one after another or together and, in the case of fuel particles, in the presence of combustion. The extent of the attrition depends on which of these breakage mechanisms is dominant. In addition, the properties of the solids such as size, surface, porosity, hardness, cracks, density, shape, and particle strength may affect the attrition rate [13]. The characteristics of the reactor, particle velocity and exposure time also play an important role. Although several authors have studied the phenomenon of attrition and proposed different models, taking into account all of these mechanisms, they have so far had limited success and there is still no general model to explain the attrition process. A much more empirical approach needs to be adopted in the study of fluidized beds [4-22], with special attention to specific materials and operating conditions. In the case of the system in Figure 1, the materials employed are mainly limestone and lime circulating in both calcination and non-calcination conditions.

Most of the studies on limestone attrition [4-22] focus on the phenomenon of attrition during calcination or during the simultaneous calcination and sulfation of CaO solids. All of these works (which are usually conducted under bubbling fluidization conditions) report that attrition is more intense during the initial calcining process. As an example, Benedetto and Salatino [18] investigated and modeled limestone attrition during calcination and sulfation at

850°C in a bubbling fluidized bed reactor. They concluded that most of the calcium lost in the form of elutriated fines came from the attrited lime while only a small amount was derived from the calcium sulfate formed after the calcination step. More recently, Jia et al.[4] studied the effect of attrition on CaO/CaCO_3 for a calcination/carbonation loop involving a circulating fluidized bed calciner and a bubbling fluidized bed carbonator. They confirmed that loss of solids by attrition was substantially reduced with the partial sulfation of the calcium oxide and observed that the extent of attrition varied for different limestones under calcining conditions and even for different limestone batches. However, attrition was always particularly intense in the initial carbonation/calcination cycles.

The aim of this work is to increase the database of attrition data on limestone under calcination conditions in a circulating fluidized bed combustor acting as calciner in a carbonation and calcination loop. We present data on the reduction in size of the sorbent particles in a 30kW test facility made up of two interconnected circulating fluidized bed reactors operating in continuous mode [26] as carbonator (CO_2 capture) and calciner (sorbent regeneration). In addition, we have tried to apply to our data, the correlations established by others authors in order to obtain the attrition constants of our solids, and we have compared it with the results reported in the literature.

2. Experimental

The experiments were conducted in a 30kW test facility built at INCAR-CSIC, consisting of two interconnected circulating fluidized bed reactors, that is described in more detail elsewhere [2,3]. Both reactors have an internal diameter of 0.1 m. The calciner and the carbonator have a height of 6 m and 6.5 m respectively. Each riser is connected to a high efficiency primary cyclone. The solids fall from the cyclone through a vertical standpipe into bubbling fluidized bed loop seals. They then flow over overflow towards an inclined

standpipe that directs them to the opposite reactor, at which point they have completed half of the solid circulation loop. Solids samples can be also extracted directly from several riser ports. A mixture of gas containing CO₂ (air from a blower and CO₂ from a Dewar) is fed into the carbonator. No air distributor is needed for these small diameter risers, so that solids can be fed in when needed. The loop seals are aerated with air.

For the purpose of the present work, the samples taken from the calciner, the carbonator and the loop seals were analysed in terms of particle size distribution.

Two limestones from the northwest of Spain were used (limestones A and B) whose activity curves showed a typical behaviour, as reported elsewhere [27]. The composition and the particle size distribution of these limestones are summarized in Table 1.. In a characteristic run, a batch of 20 kg of limestone was loaded into the loop seals and the risers. The temperatures were heated to around 600°C by electric ovens reaching half way up the risers and then the fuel was fed into the risers in order to increase the temperature to calcination conditions (above 800°C in an air fired combustor). Due to the high rates of heat loss in this small rig, several hours was needed to achieve full calcination of the initial batch of solids. As will be discussed below, attrition during the calcination of this first batch of circulating limestone was intense and small batches of fresh limestone had to be added occasionally in order to maintain the solids inventories and circulation rates which, further increased the total calcination time of the first batch of material.

Experiments with solids calcination and solids circulation without carbonation were conducted as well as carbonation-calcination experiments lasting up to 15 hours [23], with more frequent measurements of particles size distributions at suitable intervals of time from solid samples extracted from the two circulating fluidized bed reactors, from the secondary cyclones and from the solids in the standpipe of one of the cyclones. The solids samples were sieved using a vacuum sieve and a Coulter Counter so as to obtain a variation in

particle size distribution and average particle diameter after multiple calcination-carbonation cycles.

3. Results and discussion

The evolution of the limestone particle size distribution with time was closely followed during the experimentation. Gas velocities varied between 1.6 and 3 m/s and the temperatures of the solids between 600°C (650°C is usually the target in the carbonator reactor) and 940°C (temperatures higher than 800°C are characteristic in the air fired combustor that serves as calciner). Figure 2 shows the cumulative limestone particle size distributions for different accumulated circulation times. It can be observed that the longer the circulation time, the larger the weight fraction of finer particles in the circulating system. In the case of limestone A , the particle sizes of the original limestone ranged mainly between 100-400µm, 36% being fine particles (<100 µm). After 10 hours of continuous circulation, the proportion of larger particles decreased considerably, while the fine particles increased. After 40 hours of accumulated experimentation time, most of the solids left were from the original batch of 20 kg material. After this period of time, particle size distribution remained constant with time, with more than 90% of the solids being below 100 µm. The small fraction of solids with a size larger than 100 µm after 40, 84 and 133 hours probably belonged to the small batches of used limestone in the previous hours that comes from the secondary cyclons, added to compensate for the losses of material from the primary cyclons. On the other hand, in the case of limestone B, after only 8 hours of continuous circulation, the proportion of particles with a size below 100 microns was nearly 90 %, this proportion remaining almost constant during the following 15 hours of experimentation. Our objective was to study in more detail data on the first few hours of circulation, since the results obtained with limestone A had indicated the importance of attrition in the initial stages of the experiment.

The results presented in Figure 2 for limestone A clearly show the high level of attrition during the first few hours of operation time, the solids distribution remaining stable despite the attrition process. It was thought that if the system is able to cope and operate with the fine materials resulting from the intense attrition at the beginning of the cycles, then attrition should not pose a problem for the operation of the CO₂ capture loop. In the case of limestone B, more hours of experimentation will be needed to arrive at a firm conclusion, but the results obtained so far, reflect the same tendency. Nevertheless, as it was published by other authors [28], the reduction of the particle size is also attributed to CaO shrinkage, but the reduction produced by this phenomenon is negligible (less than 5%) comparing to the effect of the attrition. In order to assess the effect of attrition time, the average particle size was calculated for all the samples extracted from the calciner and carbonator for the whole experimental period, using the following expression:

$$d = \frac{1}{\sum \frac{w_i}{d_i}} \quad (1)$$

where w_i is the weight fraction of particles of average diameter d_i on the i th sieve. Figure 4 shows the evolution of the average particle size with time for the two limestones studied.

In Figure 3 (left) it can be seen that the average particle size of the samples extracted from the carbonator and the calciner decreases rapidly with time during the first 40 hours. After this initial period during which the average particle size is reduced from 178 μm to a particle size of around 90 μm , the resulting material is no longer prone to attrition and its average particle size remains almost constant for up to 140 hours of continuous circulation and/or carbonation or calcination. This is an interesting stationary point from the practical point of view, because when this is reached, the solids collected from the secondary cyclones (as a result of the small fraction of solids not captured in the primary cyclones) can be fed into the

system again without altering significantly the particle size distribution of the solids circulating in the system. The same phenomenon can be observed with limestone B (Figure 3 (right)). In this case, the average particle size of the samples extracted from the carbonator and the calciner decreases rapidly during the first 8 hours and remains constant for up to 15 hours.

It is also clear from the results in Figure 3 that the solids have been thoroughly mixed throughout the entire system, the average particle sizes in the carbonator being in most cases identical to those in the calciner. Only at a few experimental points during the first 20 hours of operation in the case of limestone A is there an indication that the solids extracted from the carbonator have an average particle size higher than the solids from the calciner. For limestone B, a similar trend can be observed, but in this case the differences between the size of the samples from the calciner and those from the carbonator are apparent throughout the entire experimental period. This is because most of the fines particles accumulate in the cyclone of the calciner. As these particles do not pass through the carbonator, their average particle size is larger than those in the calciner.

In both cases, during this initial period of operation some fresh limestone was fed into the loop-seal of the carbonator, causing a momentary increase in the average particle size of the solids extracted from the carbonator. However, in order to carry out a semiquantitative data analysis of these results using published attrition models, these potential sources of error have been ignored and all the solids are assumed to have been thoroughly mixed throughout the system and their average particle size (represented by the solid lines of Figure 4) being used for the analysis presented below.

After evaluating several of the attrition models proposed by different authors revised in the introduction and considering the type of information contained in Figures 2 and 3, we attempted to fit the available data and obtain attrition constants in order to compare our

values against those reported by other authors who employ the same models and similar experimental conditions.

A simple model to describe the evolution of the average particle size of a batch of solids in a circulating fluidized bed of lime was recently published by Chen et al.[20], who showed that average particle size varied linearly with cumulative attrition time according to the following linear relation with time:

$$\frac{d_0}{d_t} = k_a t + 1 \quad (2)$$

where d_0 is the initial average particle size, d_t is the size after the cumulative attrition time and k_a is the attrition rate constant, from which detailed semiempirical correlations can be derived [20]. It is evident that with our data, this model can only be applied to the interval during which the particle size decreases with time and not to the period where this remains constant. Therefore, from the experimental data provided in Figure 4, only the first 40 hours (in case of limestone A) were used for the application of equation 2. Figure 4 shows the fit obtained for these values, for the average particle sizes of the carbonator and the calciner as a whole.

Chen et al.[20] found the following linear relationship between the CFB attrition rate constant and the square of the excess gas velocity, $(U-U_{mf})$:

$$k_a = K_a (U - U_{mf})^2 \quad (3)$$

where both K_a ($s.m^{-2}$) and k_a (s^{-1}) are attrition rate constants. There must be a mechanical explanation related to the role of kinetic energy of the particles circulating around a loop system [5]. From the slope of the line in Figure 4, we obtained a value of k_a of $5.06.10^{-6}s^{-1}$ for limestone A and $1.44.10^{-5}s^{-1}$ for limestone B. Chen et al.[20] obtained a value of $2.42.10^{-6}s^{-1}$ under similar experimental conditions except that in their experiments the gas velocity was as high as 6 m/s, while in our experiments the average gas velocity was around 2 m/s.

Thus, in order to compare the attrition constants it was necessary to resort to the value of K_a for the system described in this work, the values obtained being $1.25 \cdot 10^{-6} \text{ s.m}^{-2}$ for limestone A and $1 \cdot 10^{-5} \text{ s.m}^{-2}$ for limestone B, both of which are substantially higher than the value of $6.72 \cdot 10^{-8} \text{ s.m}^{-2}$ obtained by Chen et al. [20].

Another simple attrition model that we used to fit the available data in this work was the first-order model proposed by Lee et al.[13] for their lime attrition data:

$$\frac{dW}{dt} = -k_a (W - W_{\min}) \quad (4)$$

where W is the weight of the parent solids in the bed (Kg), $W_{\min}$ is the minimum weight below which attrition is negligible, and k_a is the attrition rate constant (s^{-1}). Integrating this equation with the boundary conditions of $t = 0$, $W = W_0$, and $t = t$, $W = W$, we obtained the following equation:

$$\ln \left(\frac{W - W_{\min}}{W_0 - W_{\min}} \right) = -k_a t \quad (5)$$

Substituting in eq 5, the weights W , $W_{\min}$ and W_0 as a function of the diameters, the following expression was obtained (assuming spherical particles and negligible changes in density during the attrition process):

$$\ln \left(\frac{d_p^3 - d_{p\min}^3}{d_{p0}^3 - d_{p\min}^3} \right) = -k_a t \quad (6)$$

The attrition rate constant, k_a , can be obtained from the slope $\ln [(dp^3 - dp_{\min}^3)/(d_0^3 - dp_{\min}^3)]$ versus time, t in Figure 6.

The attrition rate constant, k_a , obtained from this curve is $1.85 \cdot 10^{-5} \text{ s}^{-1}$ for limestone A and $5.09 \cdot 10^{-5} \text{ s}^{-1}$ for limestone B. For a similar average gas velocity (2 m/s), Lee et al.[13] obtained a value of $3 \cdot 10^{-5} \text{ s}^{-1}$ but these results cannot be directly compared because their data were obtained under cold conditions. Furthermore, we assume their correct attrition constant to be the one derived from Fig 11 in the original paper. In the body of the

text they seem to have reported attrition constants with time units of minutes instead of seconds.

Expressing d_p as a function of d_{p0} , d_{pmin} and time,

$$d_p = \left[(d_{p0}^3 - d_{pmin}^3) \exp(-k_a t) + d_{pmin}^3 \right]^{1/3} \quad (7)$$

The data calculated from this equation, using the value of k_a obtained previously are compared with the experimental data obtained from the calciner and carbonator, in Figure 6.

As these figures show, the model represented by equation 7 is suitable for the description of the attrition process in both cases. Furthermore, the linear relationship of the model of Chen et al.[20] can be derived from equation 4 if the low values of k_a and the experimental attrition times involved are taken into account. From equation 2 it is clear that d_{pmin} can be ignored:

$$\text{If } d_{pmin} \approx 0, \ln \left(\frac{d_p^3}{d_{p0}^3} \right) = -k_a t \quad (8)$$

and expressing d_p/d_{p0} as a function of time,

$$\frac{d_p}{d_{p0}} = \exp \left(-k_a t / 3 \right) \quad (9)$$

By applying the Taylor series, eq 9 can be approximated as follows (for sufficiently low values of the product $k_a t$, as was the case in the first few hours of our experiments),

$$\frac{d_{p0}}{d_p} = k_a t / 3 + 1 \quad (10)$$

By comparing this equation with the expression obtained by Lee et al.[13], it can be seen that the attrition rate constant obtained by the latter is the constant k_a of the model proposed by Chen et al.[20] divided by 3. By applying this approach to the experimental data obtained in this work, where the k_a in Lee's model was $5.06 \cdot 10^{-6} \text{s}^{-1}$ for limestone A and $1.44 \cdot 10^{-5} \text{s}^{-1}$ for limestone B and the values of Chen's model were $1.85 \cdot 10^{-5} \text{s}^{-1}$ for limestone A and $5.09 \cdot 10^{-5} \text{s}^{-1}$ for limestone B, the relation between these two attrition models is confirmed. The third model taken from the literature to fit our experimental results was that of Cook et al.[14]. They used a second-order model for the bed mass and introduced the concept of $W_{\min}$ for very long attrition times. Thus:

$$\frac{dW}{dt} = -k_a (W^2 - W_{\min}^2) \quad (11)$$

where W is the weight of the solids in the bed, $W_{\min}$ is the minimum weight and k_a is the attrition rate constant.

In an integrated form, and after introducing suitable boundary conditions and the square dependence of k_a on $(U - U_{mf})^2$, Cook et al. obtained the following equation:

$$\frac{(U - U_{mf})^2}{2W_{\min}} \left[\ln \left(\frac{W_0 - W_{\min}}{W_0 + W_{\min}} \right) - \ln \left(\frac{W - W_{\min}}{W + W_{\min}} \right) \right] = K_a t \quad (12)$$

where W represents the ratio between the weight of the solids in the bed (W) and the initial weight (W_0) and the attrition rate constant, K_a , can be obtained from the slope of the plot of the left-hand side of the equation versus t . This attrition rate constant can also be expressed in the form of a modified Arrhenius equation:

$$K_a = K_0 \left[\frac{-E_a}{(U - U_{mf})^2} \right] \quad (13)$$

where E_a is the attrition activation energy. The slope and the y-axis intercept of the linear relationship between $\ln(K_a)$ and $-1/(U - U_{mf})^2$, gives the value of the activation energy and the frequency factor, K_0 .

The figure 7 shows a value of $1.26 \cdot 10^{-4} \text{ m}^2 \cdot \text{s}^{-3}$ for limestone A and $4.53 \cdot 10^{-4} \text{ m}^2 \cdot \text{s}^{-3}$ for limestone B. Comparing these results with the value obtained by Cook et al under similar experimental conditions, $5.27 \cdot 10^{-7} \text{ m}^2 \cdot \text{s}^{-3}$ (note that there is a typographical error in the units of K_a in the table that summarizes the overall attrition rate constants in the original paper), these K_a values again show the fragility of the two materials used in our tests, especially in the case of limestone B.

Expressing W as the ratio between the weight of the solids in the bed at each moment and the initial weight (W_0) and substituting W , $W_{\min}$ and W_0 as a function of the diameters, the following expression is obtained (assuming spherical particles and negligible changes in density in the attrition process):

$$\frac{(U - U_{mf})^2}{2 \left(\frac{d_{p \min}}{d_{p0}} \right)^3} \left[\ln \left(\frac{1 - \left(\frac{d_{p \min}}{d_{p0}} \right)^3}{1 + \left(\frac{d_{p \min}}{d_{p0}} \right)^3} \right) - \ln \left(\frac{\left(\frac{d_p}{d_{p0}} \right)^3 - \left(\frac{d_{p \min}}{d_{p0}} \right)^3}{\left(\frac{d_p}{d_{p0}} \right)^3 + \left(\frac{d_{p \min}}{d_{p0}} \right)^3} \right) \right] = K_a t \quad (14)$$

and expressing d_p as a function of d_{p0} , $d_{p \min}$ and time,

$$d_p = d_{p \min} \left[\frac{1 + \frac{d_{p0}^3 - d_{p \min}^3}{d_{p0}^3 + d_{p \min}^3} - \exp\left(\frac{2d_{p \min}^3}{d_{p0}^3 (U - U_{mf})^2} K_a t\right)}{1 - \frac{d_{p0}^3 - d_{p \min}^3}{d_{p0}^3 + d_{p \min}^3} + \exp\left(\frac{2d_{p \min}^3}{d_{p0}^3 (U - U_{mf})^2} K_a t\right)} \right]^{1/3} \quad (15)$$

Retaining the value that we previously calculated for K_a , the data obtained by this equation, can be compare with the experimental data. We thus obtain the following figures:

As in the case of the model proposed by Chen et al., this model is also suitable for the description of the attrition process experienced by the two limestones. If both models are placed side by side in the same graph (Figure 9), it can be seen that both adjustments are equally acceptable. Therefore, either of these models can be used in a carbonation-calcination loop to capture CO_2 provided that the experimental data are reliable enough to obtain the attrition constant.

4. Conclusions

Limestone particle attrition was studied in a system of two interconnected circulating fluidized bed reactors operating in continuous mode as carbonator and calciner. The results obtained with two different limestones reveals a higher attrition in the first calcination-carbonation cycles, so that the particle size (around 80-90 μm) shrinks rapidly in this initial period of time, until it reaches a stable value of particle size that remains constant for up to 140 hours in the case of one of the limestones studied. These results can be fitted to attrition models proposed by different authors, all of which are suitable and useful for interpreting and fitting the experimental data obtained in this work even though they yield different attrition constants. Having reliable experimental data for each specific limestone is essential to obtain attrition constants with these models.

Future research will need to define in more detail the relationship between the experimental attrition constant, the gas velocities and the mechanical properties of the limestone. These

can be measured independently in simple tests at a smaller scale in order to predict the attrition behaviour of sorbents on a large scale in future CO₂ capture systems.

5. Figure Captions

Figure 1. Scheme of the process for CO₂ capture from combustion flue gases using a CaO carbonation-calcination.

Figure 2. Cumulative particle size distribution for limestones A (left) and B (right).

Figure 3. Evolution of the average particle size of the solids with accumulated circulation time for the carbonator and the calciner. Figure on the left, Limestone A and figure on the right, Limestone B.

Figure 4. Ratio of initial to subsequent mean particle size as a function of time.

Figure 5. Attrition rate constant for an average gas velocity of 2 m/s.

Figure 6. Comparison of the average particle size calculated and measured in the carbonator and the calciner. Figure on the left, Limestone A and figure on the right, Limestone B.

Figure 7. Second order model for a gas velocity of 2m/s.

Figure 8. Comparison of the average particle size calculated and measured in the carbonator and the calciner. Figure on the left, Limestone A and figure on the right, Limestone B.

Figure 9. Comparison of both models. Figure on the left, Limestone A and figure on the right, Limestone B.

Acknowledgement

The financial support for this work provided by Endesa and Hunosa is gratefully acknowledged as is the individual fellowship granted to B.G by FICYT. Assistance in analyzing the size of the samples provided by I. Rodríguez is also acknowledged.

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Table 1. Composition and size distribution of the limestones investigated in this work.

Composition (wt %)	Limestone A	Limestone B
Al₂O₃	0.1	0.17
CaO	96.1	95.42
Fe₂O₃	0.2	2.64
K₂O	0.1	0.49
MgO	1.2	0.81
Na₂O	0.01	<0.01
SiO₂	1.1	0.07
TiO₂	<0.05	0.39
Size distribution (wt %)		
Dpaverage	178μm	133μm
0-36μm	1.1%	0.2%
36-63 μm	5%	10.2%
63-100 μm	30.6%	34.4%
100-200 μm	27.9%	36.3%
200-400 μm	35.4%	18.9%