Kinetics of calcination of partially carbonated particles in a Ca-looping system for CO$_2$ capture

I. Martínez*[a], G. Grasa[a], R. Murillo[a], B. Arias[b], J.C. Abanades[b]

[a] Instituto de Carboquímica, Consejo Superior de Investigaciones Científicas (CSIC), Miguel Luesma Castán 4, 50018 Zaragoza, Spain

[b] Instituto Nacional del Carbón, Consejo Superior de Investigaciones Científicas (CSIC), Francisco Pintado Fe 26, 33011 Oviedo, Spain

email: imartinez@icb.csic.es, gga@icb.csic.es, ramon.murillo@csic.es, borja@incar.csic.es, abanades@incar.csic.es

Abstract

Post-combustion CO$_2$ capture based on Ca-looping process, CaL, is a promising technology under development based on the reversible reaction between CaO and CO$_2$ to form CaCO$_3$ and the regeneration of the CaO by calcination of CaCO$_3$ in a rich CO$_2$ atmosphere. This work is focused on the study of the calcination kinetics with typical solid conditions expected in these systems. Calcination rates of carbonated materials derived from two limestones have been measured at different number of carbonation-calcination cycles, as a function of temperature and CO$_2$ partial pressure. It has been observed that calcination reaction is chemically controlled for particles below 300 µm of particle size, as internal mass transfer is negligible even under the presence of CO$_2$ in the reaction atmosphere. Calcination rate (expressed per mol of initial CaO) depends on calcination temperature and CO$_2$ partial pressure, whereas CaCO$_3$ content and/or particle lifetime do not affect the reaction rate. The basic kinetic model of Szekely et al. (1970) is shown to be valid to fit the new data. Based on these results it is shown that calcination temperatures between 880-920ºC could be sufficient to achieve nearly

1

complete calcination conversion at typical solid residence time of CFB calciner reactors

(2-3 minutes) in the CaL system.

1. Introduction.

Ca-looping process, CaL, is a rapidly developing CO_2 capture technology both in post-combustion and pre-combustion CO_2 systems (see recent reviews[1, 2, 3]). The reaction of a CaO-based sorbent with CO_2 to form $CaCO_3$ and the reverse calcination reaction (mainly in a pure CO_2 or CO_2/H_2O atmosphere) are at the core of all CaL systems.

This work focuses on the CaL system for CO_2 capture that was originally proposed by Shimizu et al.[4], using lime as CO_2-sorbent. The system involves the separation of CO_2 using the reversible carbonation reaction of CaO and the calcination of $CaCO_3$ to regenerate the sorbent. A typical configuration for this process would consist of two interconnected circulating fluidized beds (CFB), calciner and carbonator, operating under atmospheric pressure. Flue gases leaving the boiler of an existing power plant are fed into the carbonation unit where the CO_2 reacts with the CaO coming from the calciner to obtain $CaCO_3$. Solids from carbonator are sent back to the calcination unit where $CaCO_3$ is again decomposed to form CaO, which is recirculated to the carbonator, and CO_2 as a concentrated gas stream suitable for compression and storage. Since a concentrated CO_2 stream is aimed at the exit of the calciner, the equilibrium of CO_2 on CaO (close to 900ºC for pure CO_2 at atmospheric pressure) requires operation at high temperature during calcination. Oxyfuel combustion of coal can be used to supply the calcination energy (Shimizu et al.[4]) and higher efficiency options (that do not require a pure O_2 stream) have also been proposed (Martinez et al.[5] and Grasa and Abanades[6]).

Most recent studies on sorbent performance have focused on the determination of CO_2 carrying capacity of the sorbent (see reviews[1, 2, 3]) in a wide range of conditions and for

a large variety of materials. This improved knowledge on sorbent performance has facilitated the development of kinetic reaction models suitable for the conditions of interest for the process (Bouquet et al.[7], Sun et al.[8], Fang et al.[9], Grasa et al.[10]). High reaction rates between the CO_2 in the flue gas and the sorbent particles are certainly necessary in order to design compact CO_2 absorbers. The development of suitable particle reaction models has helped in the design of reactor models for the carbonation reactor in the CaL system (Alonso et al.[11], Lasheras et al.[12], Romano[13], Martínez et al.[14]). The operation of the carbonator reactor is being experimentally validated at increasing scales, from the preliminary tests carried out at the 10 kWth fluidized-bed carbonator by Abanades et al.[15] which showed the carbonation reaction of CaO as a solution to absorb the CO_2 from large stationary sources, to the 75 kWth pilot-scale dual fluidized bed system (with a bubbling fluidized bed carbonator) by Lu et al.[16] to study CO_2 capture efficiency in carbonator in fully stable and continuous mode. Charitos et al.[17] also reported on capture efficiencies above 90 % obtained in a 10 kWth dual fluidized bed facility (bubbling carbonator connected to a CFB calciner) under different operating conditions. Recently, studies carried out in a 30 kWth test facility using two interconnected CFB reactors as carbonator and calciner were presented by Alonso et al.[18] reporting capture efficiencies between 70 % and 97 % under realistic flue gas conditions. Carbonation efficiency of this CFB carbonator has been also analysed by Rodriguez et al.[19] as a function of the solid circulation rate, the solid inventory, the average carrying capacity of the CaO circulating particles, the temperature and the gas velocity in the reactor, reporting on high values in conditions close to that expected in commercial applications. Results obtained in the latest two experimental pilot plants have been validated and compared in a recent published work by Charitos et al.[20] using the active space time of both installations, with solid residence times below a few

minutes in the carbonator and calciner in most of the experiments conducted in continuous mode in the interconnected CFB reactors.

In contrast to the increasing knowledge on carbonator performance, little attention has been devoted so far to detailed analysis of the sorbent regeneration reactor coupled to the carbonator in these CaL systems. An adequate performance of this reactor is obviously essential to demonstrate CaL process viability. But it is usually assumed that this reactor (in its configuration as an oxy-fired CFB combustor) will always be able to operate (adjusting combustion conditions) at sufficiently high temperature to guarantee a very high efficiency in the calcination reaction. Recent experiments performed at a 75 kWth pilot plant by Lu et al.[16] showed that oxy-combustion of a solid fuel for sorbent regeneration in a CFB reactor allows for a good performance of the CaL process. Oxy-combustion of a fuel implies high CO_2 concentration in the calciner off-gas around 85 %vol. as well as flue gas recycle in the range of 50-60 % and therefore, this will be the environment where the regeneration of the sorbent will have to take place. A larger pilot plant facility of 200 kWth has been built at the University of Stuttgart (Hawthorne et al.[21]) to investigate the CaL process under more realistic operating conditions than in the previous lab-scale plant, where energy in the calciner is provided by combustion of CH_4 with enhanced air together with electrical heating. In this pilot plant, regenerator has been designed to operate in oxy-fuel mode by burning different types of solid fuels, mainly coal, that will provide further results to evaluate calciner performance of the CaL system. Larger plants have been proposed and built under different projects to operate the calciner under oxy-fuel combustion mode in CFB, not yet largely studied in small scale units. The biggest demonstration CaL plant (1.7 MWth) has been built in La Pereda power plant under the 7th Framework Programme project named 'CaOling' (Development of postcombustion CO_2 capture with CaO in a large testing facility,

www.caoling.eu). It is expected that this pilot plant will begin operation within the next months and will demonstrate the viability of the whole CaL process[22].

There are important issues related to the calcination of $CaCO_3$ that are specific to the CaL post-combustion technology referred above, and that have not been addressed so far in the open literature. For typical fuels and experimental conditions it is likely that the calcination environment in the oxy-fired CFB combustor acting as calciner reactor will range between 50 to 80 %vol. of CO_2[14]. Despite the effective heat recovery in CaL systems (Romeo et al.[23], Ströhle et al.[24], Hawthorne et al.[25], Martinez et al.[14]) it will always be a design target to minimize energy consumption in this reactor (Rodriguez et al.[26]) in order to minimize O_2 consumption and associated cost. Coal consumption in the calciner reactor depends on several operation and design variables of the CO_2 capture process such as the desired CO_2 capture efficiency that is determined by sorbent circulation rates between reactors and fresh sorbent addition. The design temperature in the calciner reactor will always be aimed at a value as low as possible in order to achieve not only effective calcination of $CaCO_3$ coming from the carbonator and the make up flow feed with minimum heat requirements, but also minimum dangers associated with ash issues and minimum sorbent deactivation that tends to increase drastically beyond 950ºC (Grasa and Abanades[27] and Gonzalez et al.[28]). In general, operation of the calciner at lower temperatures (around or below 900ºC in atmospheres with sufficient H_2O content) is favoured also by its proximity to standard operation of CFBC boilers (850ºC to maximize in situ SO_2 capture, see for example review of Anthony and Granatstein[29]). But at these low temperatures, the kinetics of the calcination reaction may not be sufficient to achieve the high calcination efficiencies needed in the calciner. In this context, this work is focused on the determination of the

calcination kinetics to describe the evolution of the carbonate conversion of the typical sorbent of a CaL process.

There is a wide database of literature on the thermal decomposition of $CaCO_3$ in CFBC environments (Beruto and Searcy[30], Hu and Scaroni[31], Borgwardt[32], Garcia-Labiano et al.[33], Dennis and Hayhurst[34], Rao et al.[35]) that is relevant for this purpose. Calcination kinetics of $CaCO_3$ particles is one of the most investigated inorganic reaction after combustion and has been the subject many studies in a wide range of conditions and applications. However, there is no a consensus about a general reaction mechanism[36], and for each particular application, semi-empirical models are still used for practical purposes. For desulfurization applications in flue gas combustion environments, several authors assumed that the decomposition of small limestone particles (1-90 μm) is chemically controlled (Beruto and Searcy[30], Hu and Scaroni[31], Borgwardt[32]). For larger particle sizes (below 2 mm), Dennis and Hayhurst[34] also concluded that calcination is controlled by chemical reaction at a sharp interface between $CaCO_3$ and CaO in a fluidised bed combustor. However some other works have shown evidence of the importance gained by the internal mass transfer resistance with increasing particle size (García-Labiano et al.[33]). This work will revisit these reaction models to interpret the experimental results obtained when measuring calcination rates in multi-cycled particles and CO_2 rich gas atmosphere that are characteristic of the calciner reactor in post-combustion CaL CO_2 capture systems.

2. Experimental

Carbonation and calcination cycles have been carried out in a thermogravimetric analyzer (TGA) suitable to derive reactivity data during carbonation or calcination in long multi-cycle tests. The TGA used in this work has been described in detail elsewhere[10]. The reacting gas mixture (CO_2/air) set by mass flow controllers was fed

into the bottom of a quartz tube placed into a two-zone furnace. External diffusion resistances have been eliminated operating with 2 mg of sorbent and a total gas flow of $1.11 \cdot 10^{-6}$ m^3N/s. Experiments were carried out at atmospheric pressure while temperature and sample weight were continuously recorded on a computer. For each test, sorbent underwent ten calcination/carbonation cycles (12 minutes per cycle). To avoid the decomposition of limestone during the heating up period between carbonation to calcination conditions, the carbonation reaction was carried out at 100 %vol. of CO_2 during 8 minutes and the temperature was close to that set in the calcination period. Blank tests determined possible disturbances in sample weight as a result of switching gas density in the gas flow through the reactor. At the end of each test, samples were weighted in a balance in order to check the accuracy of the TGA results and, as a result, it was observed good agreement between sorbent conversion calculated from this weight measured and that evaluated from TGA results.

Two different limestones have been used for the experiments (named A and B in the paper). Four particle size cuts have been tested for limestone A: 75-125 μm, 125-300 μm, 300-600 μm and 600-800 μm, and one size cut for limestone B: 75-125 μm. Both limestones were analysed through an ICP-OES Spectrometer to determine their chemical composition. The limestones presented a residue after loss on fusion of 56 % by weight whose mainly components were CaO, MgO and SiO_2 (see Table 1). Both limestones were characterised by using a Hg Porosimeter Quantachrome Pore Master to estimate the pore volume and the pore-size distribution and N_2 adsorption (Micromeritics ASAP2020) at 77 K was used to calculate the sorbent surface area by applying the Brunauer, Emmett and Teller equation. Results obtained in these tests together with those obtained for their calcines are shown in Table 1. The effect of three different variables has been analysed in this work: the effect of particle size, calcination

temperature and CO_2 partial pressure on multi-cycle calcination reaction. Preliminary tests were done to analyse the effect of particle size on calcination rate and elucidate the importance of gas diffusion resistances at pore level. These tests were performed for limestone A at two different CO_2 partial pressures, 0 kPa and 50 kPa. To derive the kinetic parameters for the calcination reaction including highly cycled particles (ten reaction cycles) and high CO_2 concentrations, a set of experiments was carried out analysing the effect that calcination temperature (temperatures tested ranged from 820ºC to 910ºC) and CO_2 partial pressure (from 0 kPa to 100 kPa) have on reaction rates. These tests were focused on the smallest size cut of both limestones as it will be explained in further detail below.

[Table 1]

[Figure 1]

Several tests were carried out in the TGA with larger quantities of sample, calcining at 900ºC in air, to obtain sufficient mass for measurements of pore size distribution by mercury porosimetry. Figure 1 is an example of a typical plot of dV/dD vs. pore diameter for two samples of limestone B after the first and fifth calcination respectively. It can be seen that the original texture of the first calcine with a rather narrow pore size distribution, evolves towards bimodal distribution typical of samples that have experienced several calcination-carbonation cycles[37]. These measurements were intended to aid in the selection of calcination models as will be discussed below.

In order to give an insight to the possible particle calcination reaction model for the limestones tested, a sample of fresh limestone A (75-125 µm) was half calcined at 880ºC in air and analysed by SEM. Sample preparation was carried out in an inert atmosphere, it was mildly crushed, dispersed on a graphite tab, and gold-coated with a ~20-nm-thick film for their observation under scanning electron microscopy. The

micrographs obtained by SEM are shown in Figure 2 (a) and (b) and will be used to further support the model selection in the next section.

[Figure 2]

3. Results and discussion

Preliminary measurements of calcination rates tests were carried out at different particle sizes to check the relative importance of gas diffusion effects in the different pore networks resulting from different carbonation and calcination cycles. Four particle size intervals where used (75-125, 125-300, 300-600 and 600-800 μm). Calcination temperature in these tests was fixed at around 880ºC. Two series of experiments were carried out. The first tests were conducted in absence of CO_2 in the gas fed to the TGA, so that diffusion effects of CO_2 in the pore network of the particles should be more pronounced and easier to detect when changing particle sizes. The second tests were conducted at 50 %vol. of CO_2 also for different particle sizes. Figure 3 shows the calcination curves versus time in absence of CO_2 for the calcination in the second and eighth cycle, Figures (a) and (b) respectively. As it can be seen for the second calcination, reaction rate is hardly affected by internal diffusion resistance below 300 μm or, in case internal resistance was present, its effect on kinetics would be the same for both sizes. From that size onwards, there is a small effect of particle size on calcination rate due to CO_2 internal diffusion resistance that results in a higher calcination time to achieve complete $CaCO_3$ decomposition. As limestone undergoes a higher number of calcination/carbonation cycles, the internal resistance of the CO_2 released during calcination sharply diminishes and calcination rate is practically identical even when particles as large as 600 μm diameter are used (Figure 3 b). Figure 4 shows the results from the tests carried out in presence of 50 %vol. of CO_2, which are in qualitative agreement with the results obtained when calcining in air but with

enlarged differences between curves. Although higher calcination times are required in all cases due to the effect of CO_2 on kinetics (as it will be described by reaction model equations), it is appreciated that internal mass transfer resistance continues being negligible below 300 μm of particle size from the first cycle as curves for 75-125 and 125-300 μm match up completely. For larger particle sizes (600-800 μm) calcination rates are slightly lower which can be considered a sign of both internal resistance to CO_2 diffusion in presence of CO_2 in the calcination atmosphere and reduced kinetics because of CO_2, resulting in longer time to achieve complete calcination.

[Figure 3]

[Figure 4]

From the results obtained in TGA it can be concluded that the calcination reaction of cycled particles in a CFB based post-combustion CaL system, with a particle size below 300 μm, is chemically controlled since the first cycles. This results in a reaction taking place at the same extent throughout the particles where no relevant particle size effects can be found. This homogeneous character of the reaction is even more pronounced after several calcination/carbonation cycles, as it would be expected from the opening of the pore network as noted in Figure 1. These conclusions are supported by the images obtained by SEM (Figure 2) where it is observed that pores resulted from $CaCO_3$ decomposition are uniformly distributed throughout the particle. In addition, as it has been shown recently by González et al.[38], CaL system will most likely operate with average particle sizes of CaO around 90 μm due to attrition phenomena. For all these reasons, the determination of the kinetic rate parameters for the calcination reaction models to be used in this work to interpret the available results is focused from this point on the 75-125 μm size cut.

As indicated in the introduction section, different reaction models have been proposed in the literature to describe the calcination reaction in close conditions to those used in the experiments carried out in this work. Homogeneous reaction model throughout the sorbent was assumed by Borgwardt[32] with particle sizes under 90 μm. Khinast et al.[39] applied a modified Random Pore Model, RPM, to the calcination reaction that relates the evolution of the pore structure of the solid during calcination with its conversion. The shrinking core model and the uniform conversion model appeared as suitable reaction models to describe the calcination reaction of fine particles in two extreme conditions. On the one hand, the shrinking core model would be able to describe the calcination of limestones with a very low initial porosity. On the other hand, for solids with a higher initial porosity, the uniform conversion model could be applied. This second scenario is obviously the most adequate for our results, as it has been discussed in the previous paragraphs around the observations in Figures 1-4.

Typical calcination conversion curves vs. time obtained from the multi-cycle experiments are represented in Figure 5 (a) and (b). Considering that X_{calc} and X_{carb} are the $CaCO_3$ content exiting and entering the calciner (both expressed in moles of $CaCO_3$ per mol of Ca), respectively, $(X_{carb}-X_{calc})$ is the $CaCO_3$ decomposed per mol of Ca. For the calcination of pure $CaCO_3$ (that implies 100 % of $CaCO_3$ content), $(X_{carb}-X_{calc})$ varies between 0 to 1. For the calcination of a sorbent that has been carbonated up to the maximum carrying capacity in the previous carbonation-calcination cycle, X_{N-1}, the value of $(X_{carb}-X_{calc})$ changes from 0 to X_{N-1}.

[Figure 5]

According to Figure 5 calcination rates (slopes of $d(X_{carb}-X_{calc})/dt$ for $(X_{carb}-X_{calc}) < X_{N-1}$) are constant with different cycle number for a given calcination temperature and CO_2 concentration in the gas phase. However, in order to facilitate the interpretation of the

experimental results with a definition of conversion independent of cycle number, the $CaCO_3$ decomposed on every cycle has been normalised with the maximum carbonate content achievable in the previous cycle as follows:

$$f_{calc} = \frac{moles\ of\ CaCO_3\ decomposed}{moles\ of\ CaO \cdot X_{N-1}} = \frac{(X_{carb} - X_{calc})}{X_{carb}} \qquad (1)$$

In this way, f_{calc} ranges on every cycle from 0 to 1. The evolution of X_{N-1} (or X_N) with N has been widely studied, and it has been found that can be described according to Equation 2 for a variety of limestones and reaction conditions, with a deactivation constant k of 0.52 and a sorbent residual molar conversion X_r of 0.075[27].

$$X_N = \frac{1}{\frac{1}{(1-X_r)} + kN} + X_r \qquad k=0.52,\ X_r=0.075\ (T_{calc} < 950°C,\ t_{calc} < 20\ min) \qquad (2)$$

Figure 6 represents the normalisation of the experimental conversion data for the conversion curves included in Figure 5 (a) and (b).

[Figure 6]

The resulting plots can then be fitted to a kinetic model for calcination embracing the observations reported in previous paragraphs. As indicated above, the materials tested in this work follow during calcination an apparent homogeneous conversion pattern at particle level. Fang et al.[40] proposed an equation based on the classic grain model of Szekely and Evans[41] to describe the calcination reaction of CaO-based sorbents in CaL applications, that is in principle consistent with an homogeneous model at particle level:

$$\frac{df_{calc}}{dt} = k_{c,N} \cdot (1 - f_{calc})^{2/3} \cdot (C_{eq} - C_{CO2}) \qquad (3)$$

In this model, each carbonated particle is assumed to be formed by uniformly sized nonporous spherical grains of $CaCO_3$ and CaO that calcine following a shrinking core model under chemical reaction control (Equation 3). A similar expression was also used to fit fast carbonation rates in a previous work (Grasa et al.[42]), although more elaborate

versions of this carbonation model have been published more recently (Grasa et al.[10]) based on RPM (developed by Bathia and Perlmutter[43-44]) to account for slow reaction regimes and transitions regimes. We have attempted data fit with equation 3 in this work because of its simplicity and sufficient good quality of the fit for the whole range of calcination curves. Furthermore, it is already known that grain model predictions match those made by the RPM under chemical reaction control and, as well, when moderate transport resistances are included for porous particles with typical values of reaction surface area, total pore length and porosity[43-44].

Equilibrium CO_2 concentration (C_{eq}) has been evaluated from the molar fraction of CO_2 in the equilibrium, f_e, by using Equation 4 where T is the operation temperature (in ºK) and P is the total system pressure (in atm)[45].

$$f_e = \frac{10^{(7.079 - 8308/T)}}{P} \tag{4}$$

To determine the kinetic parameter of the calcination reaction, different experiments including up to 10 calcination/carbonation cycles each, have been carried out for both limestones varying the calcination temperature from 820 to 910ºC, and reaction atmosphere from 0 kPa to 100 kPa of CO_2. The calcination conversion of limestone particles on each cycle N, was calculated from the experimental data on weight changes measured with the TGA analyser during reaction according to Equation 1, normalized with the maximum carbonate content achievable in the previous cycle. Combining Equations 1 and 3, calcination rate (per mol of Ca) will be given by:

$$\frac{d(X_{carb} - X_{calc})}{dt} = k_c \left(1 - \left(\frac{X_{carb} - X_{calc}}{X_{carb}}\right)\right)^{2/3} \cdot (C_{eq} - C_{CO2}) \tag{5}$$

A fitting exercise has been carried out to determine kinetic constant of calcination reaction k_c, using experimental results obtained in the TGA set up described in the experimental section. The kinetic constant was determined in each cycle from the

13

conversion curves at different calcination temperatures. An Arrhenius representation was plotted for the individual values of k_c obtained and pre-exponential factor, k_{c0} (m^3/kmol·s), and activation energy, E_{ac} (kJ/mol), were determined from the ordinate in the origin and the slope, respectively, according to Equation 6.

$$k_c = k_{c0} \cdot \exp\left(\frac{-E_{ac}}{R \cdot T}\right) \tag{6}$$

The values of k_{c0} and E_{ac} have been included in Table 1 for both limestones. Activation energies obtained over the temperature range 820 to 910ºC for Limestone A, 112.4 kJ/mol, and Limestone B, 91.7 kJ/mol, are similar and as it could be expected as both limestones had similar internal structure and pore size evolution pattern. These activation energies are somehow in the lower range of those reported in the literature, between 110 to 210 kJ/mol (Gallagher and Johnson[46], Borgwardt[32], Garcia-Labiano et al.[33], Dennis and Hayhurst[34], Rao et al.[35]) obtained for temperatures in a range of 600 to 900ºC However they are in close agreement with values obtained by García-Calvo et al.[47] and Romero-Salvador et al.[48] who reported activation energies for calcite decomposition of around 109 kJ/mol and stated this low value was due to the presence of impurities and/or physical processes, such as sintering. The limestones tested in this work present at least 4 %wt. of impurities, that could act as catalyst and result in slightly low activation energies. The fact that Limestone B present higher amount of impurities than Limestone A could also explain its lower activation energy with respect to the other limestone. But it is beyond the scope of this work to explain in more detail the source of these variations in apparent activation energies, because from a practical point of view it is sufficient to have for each limestone a suitable set of pre-exponential factor and activation energy for equation 5.

[Figure 7]

Figure 7 shows the effect of calcination temperature on reaction rate for limestone B during fifth calcination in absence of CO_2 (Figure a) and in presence of 25 kPa of CO_2 (Figure b). As expected, this figure shows how increasing calcination temperature results in a higher reaction rate, and also that the presence of CO_2 reduces the reaction rate for a given temperature. CO_2 partial pressures close to those given by the equilibrium (Equation 4) result in a dramatic reduction in reaction rate. This is the case of calcination temperature at 825ºC under a 25 kPa of CO_2 partial pressure in the reaction atmosphere that lead to a complete calcination times well above 2 min.

With respect to the dependence of the calcination reaction with the presence of CO_2, the right hand side term in Equation 3 or 5 has been applied in the past with success by several authors to describe this dependence (Hu and Scaroni[31], Rao et al.[35], Silcox et al.[49], Fuertes et al.[50]). Figure 8 shows the effect of CO_2 partial pressure on calcination rates for a given temperature (890ºC in this case) and for both limestones. Figure 8 (a) represents the calcination conversion of a cycle number 2 for limestone A. Figure 8 (b) represents the calcination conversion of a cycle number 5 for limestone B.

[Figure 8]

The model also presents good agreement between prediction and experimental data under calcination conditions close to the equilibrium as it can be seen in Figure 9. The difference between the molar fraction of CO_2 given by the equilibrium composition (f_e) and the CO_2 in the reaction atmosphere (f_{CO2}) has been varied between 0.05 and 0.08 for limestone B for two different temperatures. This is an indirect validation of the accuracy of the equation of Baker[45] (equation 4) for the equilibrium in this temperature range and the accuracy of the experimental set up (sample temperatures in the TG plate and gas composition).

[Figure 9]

Despite of its simplicity, the model predictions represented in Figures 6 to 9 by solid lines reproduce with reasonable accuracy all the experimental data presented in this work. The model proposed is able to predict the calcination conversion of the sorbent in a range of conditions of interest for the CaL process and different calcination/carbonation cycles. Furthermore, the integration of equation 5 provides an expression for evaluating the full calcination time (t^*_c) needed to achieve complete decomposition of $CaCO_3$ (or what is the same, to achieve 0 % of $CaCO_3$ content) for particles of any $CaCO_3$ content X_{carb} that yields:

$$t^*_c = \frac{3 \cdot X_{carb}}{k_c \cdot \left(C_{eq} - C_{CO2}\right)} \tag{7}$$

[Figure 10]

Figure 10 represents this full calcination time, t^*_c, for some illustrative examples using the limestone A kinetic data. As can be seen with the lines with symbols, calcination of pure limestone would require a substantial reaction time and/or higher temperatures of calcination for a given ambient partial pressure of CO_2 and temperature. However, the calcination of typical solids from the carbonator (with a molar carbonate content of 15 % in the example of this figure) requires much lower calcination times. This may have important positive implications for the CaL system. As it has been discussed in the introduction, calcination temperature has a great influence in the energy requirements of the CaL system and therefore in the economics. It is observed from Figure 10 that even temperature below 900ºC are clearly enough for achieving complete calcination under CO_2 concentrations typical of the CaL calcination environment at residence times typical in the circulating fluidised bed calciner. Therefore, lower temperatures than expected in previous simulation publications (Shimizu et al.[4], Martínez et al.[5], Lasheras et al.[12], Romano[13], Martínez et al.[14], Ströhle et al.[24], Hawthorne et al.[25], Rodriguez et al.[26], Yongping et al.[51],) could be considered. Coal and oxygen consumption could be

16

optimised, SO_2 capture in the calciner gets closer to the optimum conditions and a wider variety of fuels (ash softening issues) can be used in the calciner at lower calcination temperatures.

4. Conclusions

Calcination kinetics of two different limestones that have experienced repetitive calcination/carbonation cycles have been determined in a TGA analyser. It has been experimentally observed that the calcination reaction is chemically controlled as internal mass transfer resistance is negligible up to 300 μm particle size, even in presence of CO_2 in the reaction atmosphere. In this way, calcination reaction (expressed per mol of initial CaO) depends on calcination temperature and CO_2 partial pressure, whereas $CaCO_3$ content and/or particle lifetime do not affect the reaction rate. The calcination reaction in multi calcination/carbonation cycles has been described with a reaction model based on a grain model that considers a particle formed by grains that follow a shrinking core model under chemical reaction control and the kinetic constant of the reaction has been determined. The model proposed is able to predict the calcination conversion of the sorbent at calcination conditions of interest for the Ca-looping process and should contribute to its scaling up.

Nomenclature

C_{CO2} (kmol/m^3): Concentration of CO_2 in the gas phase

C_{eq} (kmol/m^3): Equilibrium concentration of CO_2 in the gas phase

E_{ac} (kJ/mol): Activation energy of kinetic constant of $CaCO_3$ calcination

f_{calc}: Fraction of $CaCO_3$ decomposed to CaO and CO_2 in the calcination reaction with reference to the moles of $CaCO_3$ coming from former carbonation (it varies from 0 to 1 in every cycle)

f_{CO2}: Molar fraction of CO_2 in the gas phase

f_e: Molar fraction of CO_2 in the equilibrium (according to Baker[42])

k: Deactivation constant of CaO

k_c (m^3/kmol·s): Kinetic constant of $CaCO_3$ calcination

k_{c0} (m^3/kmol·s): Pre-exponential factor of kinetic constant of $CaCO_3$ calcination

N: Number of calcination/carbonation cycles

P: Pressure

p_{CO2}: CO_2 partial pressure

R (J/mol·K): Ideal gas constant

T: Temperature

t_c^* (s): Time needed to achieve full calcination for a particle of any $CaCO_3$ content

X_{calc} (moles $CaCO_3$/mol Ca): $CaCO_3$ content exiting the calciner

X_{carb} (moles $CaCO_3$/mol Ca): $CaCO_3$ content entering the calciner:

X_r: Residual conversion of CaO after many hundred cycles

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) Dean, C.C.; Blamey, J.; Florin, N.H.; Al-Jeboori, M.J.; Fennell, P.S. *Chem. Eng. Res. Des*. **2011**, 89, 836-855.

(4) Shimizu, T.; Hirama, T.; Hosoda, H.; Kitani, K.; Inagaki, M.; Tejima, K. *Trans. IChemE*. **1999**, 77 (Part A), 62-68.

(5) Martínez, I.; Murillo, R.; Grasa, G. Rodríguez, N.; Abanades, J.C. *Int. J. Greenhouse Gas Control*. **2011**, 5, 498-504.

(6) Grasa, G.; Abanades, J.C. *Chem. Eng. Sci*. **2007**, 62, 619-626.

(7) Bouquet, E.; Leyssens, G.; Schönnenbeck, C.; Gilot, P. *Chem. Eng. Sci*. **2009**, 64, 2136-2146.

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

(9) Fang, F.; Li, Z.S.; Cai, N.S. *Energy Fuels*. **2009**, 23, 207-216.

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

(11) Alonso, M.; Rodríguez, N.; Grasa, G.; Abanades, J.C. *Chem. Eng. Sci*. **2009**, 64, 883-891.

(12) Lasheras, A.; Ströhle, J.; Galloy, A.; Epple, B. *Int. J. Greenhouse Gas Control*. **2011**, 5, 686-693.

(13) Romano, M. *Energy Procedia*. **2009**, 1, 1099-1106.

(14) Martínez, I.; Murillo, R.; Grasa, G.; Abanades, J.C. *AIChE J*. **2011**, 57 (9), 2599-2607.

(15) Abanades, J.C.; Anthony, E.J.; Lu, D.Y.; Salvador, C.; Álvarez, D. *AIChE J*. **2004**, 50 (7), 1614-1622.

(16) Lu, D.Y.; Hughes, R.W.; Anthony, E.J. *Fuel Process. Technol*. **2008**, 89, 1386-1395.

(17) Charitos, A.; Hawthorne, C.; Bidwe, A.R.; Sivalingman, S.; Schuster, A.; Spliethiff, H.; Scheffknecht, G. *Int. J. Greenhouse Gas Control*. **2010**, 4, 776-784.

(18) Alonso, M.; Rodríguez, N.; González, B.; Grasa, G.; Murillo, R.; Abanades, J.C. *Int. J. Greenhouse Gas Control*. **2010**, 4, 167-173.

(19) Rodríguez, N.; Alsono, M.; Abanades, J.C. *AIChE J*. **2011**, 57 (5), 1356-1366.

(20) Charitos, A.; Rodríguez, N.; Hawthorne, C.; Alonso, M.; Zieba, M.; Arias, B.; Kopanakis, G.; Scheffknecht, G.; Abanades, J.C. *Ind. Eng. Chem. Res*. **2011**, 50, 9685-9695.

(21) Hawthorne, C.; Dieter, H.; Bidwe, A.; Schuster, A.; Scheffknecht, G.; Unterberger, S.; Käβ, M. *Energy Procedia*. **2011**, 4, 441-448.

(22) Sánchez-Biezma, A.; Ballesteros, J.C.; Díaz, L.; de Zárraga, E.; Álvarez, F.J.; López, J.; Arias, B.; Grasa, G.; Abanades, J.C. *Energy Procedia*. **2011**, 4, 852-859.

(23) Romeo, L.M.; Abanades, J.C.; Escosa, J.M.; Paño, J.; Giménez, A.; Sánchez-Biezma, A.; Ballesteros, J.C. *Energy Convers. Manage*. **2008**, 49, 2809-2814.

(24) Ströhle, J.; Galloy, A.; Epple, B. *Energy Procedia*. **2009**, 1, 1313-1320.

(25) Hawthorne, C.; Trossmann, M.; Galindo Cifre, P.; Schuster, A.; Scheffknecht, G. *Energy Procedia*. **2009**, 1, 1387-1394.

(26) Rodríguez, N.; Alonso, M.; Grasa, G.; Abanades, J.C. *Chem. Eng. J*. **2008**, 138, 148-154.

(27) Grasa, G.; Abanades, J.C. *Ind. Eng. Chem. Res*. **2006**, 45, 8846-8851.

(28) González, B.; Grasa, G.S.; Alonso, M.; Abanades, J.C. *Ind. Eng. Chem. Res*. **2008**, 47, 9256-9262.

(29) Anthony, E.J.; Granatstein, D.L. *Prog. Energy Combust. Sci*. **2001**, 27, 215-236.

(30) Beruto, D.; Searcy, A.W. *J. Chem. Soc., Faraday Trans. 1*. **1974**, 70, 2145-2153.

(31) Hu, N.; Scaroni, A.W. *Fuel*. **1996**, 75 (2), 177-186.

(32) Borgwardt, R.H. *AIChE J*. **1985**, 31 (1), 103-111.

(33) Garcia-Labiano, F.; Abad, A.; de Diego, L.F.; Gayán, P.; Adánez, J. *Chem. Eng. Sci*. **2002**, 57, 2381-2393.

(34) Dennis, J.S.; Hayhurst, A.N. *Chem. Eng. Sci*. **1987**, 42 (10), 2361-2372.

(35) Rao, T.R.; Gunn, D.J.; Bowen, J.H. *Chem. Eng. Res. Des*. **1989**, 67, 38-47.

(36) L'vov, B.V.; Polzik, L.K.; Ugolkov, V.L. *Thermochim. Acta*. **2002**, 390, 5-19.

(37) Alvarez, D.; Abanades, J.C. *Ind. Eng. Chem. Res*. **2005**, 44, 5608-5615.

(38) González, B.; Alonso, M.; Abanades, J.C. *Fuel*. **2010**, 89, 2918-2924.

(39) Khinast, J.; Krammer, G.F.; Brunner, Ch.; Staudinger, G. *Chem. Eng. Sci*. **1996**, 51 (4), 623-634.

(40) Fang, F.; Li, Z.S.; Cai, N.S. *Energy Fuels*. **2009**, 23, 207-216.

(41) Szekely, J.; Evans, J.W. *Chem. Eng. Sci*. **1970**, 25, 1091-1107.

(42) Grasa, G.; Abanades, J.C.; Alonso, M.; González, B. *Chem. Eng. J*. **2008**, 137, 561-567.

(43) Bathia, S.K.; Perlmutter, D.D. *AIChE J*. **1980**, 26 (3), 379-386.

(44) Bathia, S.K.; Perlmutter, D.D. *AIChE J*. **1981**, 27 (2), 247-254.

(45) Baker, R. *J Appl. Chem. Biotechnol*. **1973**, 23, 733-742.

(46) Gallagher, P.K.; Johnson, D.W. *Thermochim. Acta*. **1973**, 6, 67-83.

(47) García-Calvo, E.; Arranz, M.A.; Letón, P. *Thermochim. Acta*. **1990**, 170, 7-11.

(48) Romero-Salvador, A.; García-Calvo, E.; Benitez Aparicio, C. *Thermochim. Acta*. **1989**, 143, 339-345.

(49) Silcox, G.D.; Kramlich, J.C.; Pershing, D.W. *Ind. Eng. Chem. Res*. **1989**, 28, 155-160.

(50) Fuertes, A.B.; Marbán, G.; Rubiera, F. *T. I. Chem. Eng-Lond*. **1993**, 71 (A), 421-428.

(51) Yongping, Y.; Rongrong, Z.; Liqiang, D.; Kavosh, M.; Patchigolla, K.; Oakey, J. *Int. J. Greenhouse Gas Control*. **2010**, 4, 603-612.

FIGURES

Figure 1. Pore size distribution for limestone B after first and fifth calcination of the sorbent.