

Experimental validation of the calcium looping CO₂ capture process with two circulating fluidized bed carbonator reactors

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ABSTRACT

Postcombustion CO_2 capture using CaO as a regenerable solid sorbent in a circulating fluidized bed (CFB) carbonator is emerging as a promising CO_2 capture technology. Experimental validation of this concept is provided through a comparative analysis of the results obtained in two laboratory-scale dual fluidized bed (DFB) installations located at INCAR-CSIC (Spain) and IFK (Germany). The analysis is

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focused on the performance of the CFB carbonator reactors operated with continuous solid circulation of CaO. A reasonable closure of the carbon balances (i) between the CO₂ that has disappeared from the gas phase, (ii) the CaCO₃ circulating between the reactors and (iii) the CaCO₃ that is formed within the carbonator bed has been established. A necessary condition for the capture of a given molar flow of CO_2 is experimentally demonstrated and requires that a slightly over-stoichiometric molar flow of active CaO is supplied to the carbonator. The deactivation behavior of the sorbents during continuous looping conditions has been measured. The key parameter to interpret the carbonator reactor results has been the active space time, that is indicative of the CaO inventory per molar flow of CO₂ participating in the carbonation reaction and of the reaction rate of the solid inventory in the reactor. Two different approaches have been utilized in order to find a suitable expression for this parameter, thus achieving its correlation with the CO₂ capture efficiency. A simple model assuming instant mixing of solids and plugflow of the gas has been tested. Based mainly on carbonator active space time variation, the CO₂ capture efficiency are shown to lie between 30 % and above 90 %. These results confirm the technical viability of the calcium looping postcombustion CO₂ capture process. They have been used for designing the current pilot-plant facilities which are scaled up 20-50 times in regard to the lab-scale units. Moreover, the lab-scale results obtained allow for simulation work to be initiated in regard to the full scale Ca looping application.

KEYWORDS: CO₂ capture, calcium looping, carbonation, circulating fluidized bed, CaO

INTRODUCTION

Postcombustion CO_2 capture technologies using CaO as a regenerable solid sorbent have emerged as a promising route to reduce electricity penalty and cost of CO_2 capture from flue gases of both new and existing power plants (see recent reviews by Anthony¹ and Blamey et al.²). The process consists of two fluidized bed reactors connected by solid transport pipes and makes use of the reversible carbonation reaction of CaO and the subsequent calcination of the CaCO₃ formed. A CO₂-lean gas exits the

carbonator and is released to the atmosphere. The produced $CaCO_3$ is transported to the regenerator where the calcination reaction takes place in order to regenerate the CaO and produce a pure CO_2 stream. The CaO produced is transported back to the carbonator to further capture flue gas CO_2 , while the CO_2 released from the regenerator can be directed to purification, compression and storage.

There are now hundreds of research papers that have investigated different important aspects of calcium looping processes, including sorbent performance properties (decay in sorbent capacity along the carbonation-calcination cycles, operation mapping at different temperatures and pressures, CaO reactivity towards CO₂, SO₂, etc.), sorbent improvement methods, reactor and process modeling, energy integration schemes and techno-economic studies of the full system. However, the experimental information validating the concept is still relatively recent and remains scarce.

Successful tests with regard to calcium looping were conducted as early as 1967 ³ in a pilot plant developed for the "Acceptor" process, involving a dual fluidized bed (DFB) reactor system, consisting of a gasifier-acceptor and a combustor-calciner operating at very high pressures and temperatures. Recently, rapid progress has been achieved regarding the adsorption enhanced reforming (AER) process. Koppatz et al. ⁴ reported results on hydrogen production by means of steam gasification of biomass in the presence of CaO in an 8 MW (input) DFB facility operating at atmospheric pressure. Moreover, IFK has recently operated a 200 kW_{th} DFB facility at AER conditions and achieved a hydrogen product gas concentration of 72 Vol.-% for 18 h at $650^{\circ}C^{5}$. In addition, a novel biomass two-stage gasification process has been conceived that is also based on CO₂ adsorption from a Ca sorbent which is able to achieve higher biomass utilization and hydrogen concentration than the AER process⁶. Although, these experiences and developments in regard to the precombustion route are valuable to support the practical viability of calcium looping systems, it is obvious that the boundary conditions for the postcombustion calcium looping application are very different. In principle, the atmospheric conditions and low partial pressures of CO₂ in a combustion flue gas, which keep on decreasing as CO₂ is being captured in the

reactor, make the effective adsorption of CO_2 by CaO more challenging. Only recently, some test results in small circulating fluidized bed reactors have been reported for postcombustion CO_2 capture, operated in CFB mode which is close to expected industrial applications.

Alonso et al. ⁷ and Rodríguez et al.⁸ carried out experimental work at the 30 kW_{th} INCAR-CSIC plant, which includes a CFB carbonator coupled with a CFB regenerator, and reported CO₂ capture efficiencies between 70 and 97% under realistic CFB carbonator operation conditions. Charitos et al. ⁹ performed continuous experimental tests of CO₂ capture with CaO at the 10 kW_{th} IFK facility, utilizing a BFB carbonator and a CFB regenerator. They conducted a parametric study to define the link of main process operational variables and the carbonator CO₂ capture efficiency. Recently, the IFK facility was operated with use of its CFB as the carbonator, since this is more representative of the industrial setting. The focus of this paper is to present a comparative analysis of the methodologies and results obtained in the two CFB carbonators of the DFB lab-scale facilities in Spain and Germany regarding the testing of the postcombustion calcium looping concept. It is the outcome of more than five years of common development work regarding reactor design, operation and result interpretation.

EXPERIMENTAL METHODS

General schemes of the INCAR-CSIC and IFK facilities considered in this work have been shown elsewhere ^{7, 9} and are not presented in detail here. The key characteristics of the units are summarized in Table 1. Figure 1 shows a schematic representation of the carbonator reactors of both facilities and their key mass flows. A molar flow of CO_2 (F_{CO2}) enters the carbonator along with other gas components (F_{gas}). A percentage of the CO_2 molar flow, expressed by the CO_2 capture efficiency (E_{carb}), is captured from the bed inventory (n_{Ca}), while CO_2 lean gas is emitted to the atmosphere. The CaO inventory within the carbonator is distributed between three main fluid-dynamic regions, as has been indicated by a scaled cold model¹⁰ and modelling study¹¹ aimed at the calcium looping postcombustion process. These include the dense region, the lean core-annulus region and the exit region and affect the carbonator performance due to their different solid fractions and gas-solid contacting characteristics. The riser entrainment exiting the reactor is separated from the cyclone separator and can either be split between two streams, i.e. the first circulates internally within the carbonator riser while the second is directed to the regenerator, or it can be fully directed to the regenerator depending on the DFB system design. In the IFK case such a solid split arrangement is controlled by a cone valve⁹⁻¹⁰, while in the INCAR-CSIC case, the riser entrainment can only be directed to the regenerator. A molar flow of CaO circulates between the reactors (F_{Ca}) in order to provide the carbonator with calcined material for CO₂ capture. The carbonation conversion of the solid stream exiting and entering the carbonator is termed as X_{carb} and X_{cale} (X_{carb} > X_{cale}), respectively. Therefore, the X_{carb} and X_{cale} are expressed in mol CaCO₃/mol Ca.

The INCAR-CSIC carbonator riser height is 6.5 m, while that of IFK is 12.4 m. The internal riser diameter of the INCAR-CSIC, IFK carbonators is 100 mm and 70 mm, respectively. Both DFB units are electrically heated and are equipped with pressure transducers and thermocouples in order to obtain the respective pressure profiles and carry out solid inventory estimations.

When considering the differences of the operational velocities of the two units, namely 1.5-3.5 m/s for the INCAR-CSIC riser and 4.0-6.0 m/s for the IFK riser, two aspects can be highlighted. The first is that the flow of synthetic flue gases entering the INCAR-CSIC carbonator could have been produced by a firing system of 30 kW_{th}, while the corresponding firing system for the IFK carbonator would have been in the 10-15 kW_{th} range. Besides CO₂, the synthetic flue gas consists of air in the case of INCAR-CSIC and N₂ in the case of IFK. The second aspect is that the two carbonators operate in two neighbouring fluidization regimes, namely the turbulent and the fast fluidization regime, when considering the INCAR-CSIC and IFK carbonator, respectively. This can be identified in the fluid-dynamic regime map of Bi and Grace¹². The different fluidization regimes at which the carbonators operate justify the large differences in riser entrainment values, i.e. 1-4 kg/m²s for the INCAR-CSIC carbonator and 10-

20 kg/m²s for that of IFK. In addition, the range of the key parameter of calcium looping ratio (F_{Ca}/F_{CO2}) differs between the two facilities. In the case of the INCAR-CSIC facility, the F_{Ca}/F_{CO2} range is 5-10, while in the IFK facility it is 3-20. The F_{Ca}/F_{CO2} values of the INCAR-CSIC CFB carbonator can be controlled through riser fluidization measures and loop seal aeration. No internal recirculation is required (see Figure 1) since obtained Gs values correspond to the desired F_{Ca}/F_{CO2} values. This is not true for the IFK case, due to the very large Gs values associated with the fast fluidization regime. Therefore, internal recirculation is necessitated in combination with a cone valve to control the F_{Ca}/F_{CO2} value. Otherwise, the F_{Ca}/F_{CO2} range for the IFK facility, if internal recirculation was omitted, would have been in the range of 20-60. Such high F_{Ca}/F_{CO2} are unnecessary, are associated to high heat requirements¹³ in the regenerator of an industrial facility and thus to high oxygen consumption and $cost^{14}$. Alternative methods to the utilization of internal recirculation in order to control the F_{Ca}/F_{CO2} ratio have been suggested in DFB systems utilized for other applications, i.e. biomass steam gasification¹⁵ and chemical looping combustion¹⁶. These include variation of the facility total solid inventory or partitioning of the riser flow stream in a primary and secondary fraction. However, they are unsuitable for the case of the IFK system for facility specific and process related reasons: (i) scaled cold model testing¹⁰ has shown that variation of the total solid inventory has a minor effect on the riser entrainment. (ii) partitioning of the flue gas in a primary and a secondary gas stream would mean that part of the flue gas would "avoid" the dense bed carbonator region which is sorbent rich. Finally, it has to be underlined that the greatest merit of utilizing internal recirculation is that it decouples carbonator inventory and riser velocity from the F_{Ca}/F_{CO2} value which can than be set independently.

Other minor differences between INCAR-CSIC and IFK are related to experimental procedure. These include the way that solid sampling and circulation rate measurements are carried out. In the case of INCAR-CSIC, the solid samples used for TG analysis are taken from axial reactor ports, while in the case of IFK they are taken from the loop seal directly after the corresponding reactor exit. Regarding solid circulation rate measurements used to derive the riser G_s and F_{Ca}/F_{CO2} values, INCAR-CSIC diverts the solid flow to a dead volume for a given period of time and than measures the weight of the

collected solids, while IFK measures the particle bed height of accumulating solids in a quartz glass standpipe segment, once the aeration of the corresponding loop seal is shut off.

INCAR-CSIC has carried out experiments using two different high purity limestones from the North of Spain that presented very similar chemical behaviors with an average original particle size of 130 and 180 μ m. IFK has used two particle size distributions (PSDs) of a German limestone from the Swabian Alb region with an average particle size of 350 μ m and 170 μ m. Chemical composition of the limestones used have been reported elsewhere ^{9, 17}. Figure 2 shows the decay of their CO₂ carrying capacity (X_N) with increasing cycle number (N), as recorded with use of the INCAR-CSIC TG analyzer under same carbonation-calcination conditions. As has been analyzed in many previous publications, the X_N is defined as the X_{carb} value at which the carbonation reaction shifts from the fast kinetically controlled regime to the slow diffusion controlled regime¹². Therefore, X_N is also expressed in mol CaCO₃/mol Ca. From this data, it is apparent that the decay of the X_N of the German limestone is slightly more pronounced than that of the Spanish limestones.

Although the regenerator (calciner reactor) is not the subject of this study, it is relevant to note that the regenerator conditions can influence the carbonator reactor performance, not only through the obvious impact on calcination conversion, but trough the possible deactivation phenomena influencing the sorbent CO_2 carrying capacity. However, the calcination conditions have been similar between the two installations, since the regeneration temperature has been around 900°C and the sorbent residence time range is similar and in the range of 1-5 min. Air-fired coal combustion is utilized to supply additional heat to that provided by electrical heating in the INCAR-CSIC regenerator, while CH_4 combustion with O_2 (40 vol.-%) enhanced air is realized in the IFK regenerator. Future large scale systems will operate the regenerator in coal oxy-fuel combustion mode, not yet tested in these small laboratory scale units.

RESULTS AND DISCUSSION

The experimental results presented here are derived from steady-state conditions only. A steady state is defined as the situation where carbonator temperatures, pressure drops, inlet gas flows and outlet gas phase concentrations remain constant for a period of time of at least 10 minutes. A pre-requisite for the above is that the regenerator also operates under steady state conditions which can be defined in the same sense, thus providing the carbonator with a constant amount of regenerated CaO. Once steady state operation is achieved, the only intervention required is the addition of small amounts of sorbent (fresh pre-calcined bed material or extracted bed material removed from the DFB system during solid sampling) in order to maintain a constant reactor inventory since some is lost over time due to attrition and/or cyclone inefficiencies. In regard to the carbonator, each experimental steady state period is characterized by a given set of distinctive parameters. These originate from continuous measurements and from TG analysis of solid samples extracted. They include: (i) its average temperature (T_{carb}), (ii) sorbent inventory (n_{Ca}), calculated from the reactor pressure drop, (iii) inlet CO₂ concentration, (iv) outlet CO₂ concentration, (v) the carbonate content of exiting solids (X_{carb}), (vi) the carbonate content of entering solids (X_{calc}), i.e. that of the solids exiting the regenerator, (vii) the net carbonation conversion $(\Delta X = X_{carb} - X_{calc})$ occurring within the carbonator, (viii) the average CO₂ carrying capacity (X_{ave}) of the reactor inventory and finally (ix) the active space time (τ_{active}). The X_{ave} represents the maximum carbonation conversion that can be achieved by the average solid in the carbonator at the end of the fast reaction period. It is estimated in a standard thermo-gravimetric carbonation test¹⁸, regarding the solid samples extracted from the carbonator. Finally, the explanation of the physical meaning and the derivation of the active space time is presented later in this work.

Closure of carbon mass balances

The methodology to interpret experimental results is similar in the two rigs. The experimental information is first validated with the closure of the carbon mass balance, given in equation (1). This involves the experimental measurement of the inlet and outlet gas flows, concentrations and the solid flow entering and leaving the carbonator reactor as depicted in Figure 1.

$$F_{CO2}E_{carb} = F_{ca}(X_{carb} - X_{calc})$$
(1)

The two installations are able to report reliable CO₂ capture efficiency values measured from the gas phase as the CO₂ disappearing is continuously measured by gas analyzers. Furthermore, the calcium looping rate (F_{Ca}) is measured, while the carbonation conversion difference ($X_{carb}-X_{calc}$) is determined independently through TG analysis. The closure of the mass balance of equation (1) has been shown elsewhere¹⁹ to be sufficient for both data sets of INCAR-CSIC and IFK. In some experiments, the IFK carbonator has achieved high carbonator cross-section specific CO₂ throughputs, i.e. $F_{CO2}E_{carb}/A_{carb}$ values, closer to what is expected for large-scale application, i.e. > 6 mol/m²s.

Another way to express the goodness of the closure of the carbon mass balance is to take into account the active flow of CaO exiting the regenerator and entering the carbonator, $F_{Ca}(X_{ave}-X_{calc})$, and the molar flow of CO₂ being captured, i.e. $F_{CO2}E_{carb}$. The X_{ave} represents the average X_N of the carbonator particles, since they have different histories within the calcium looping facilities. A necessary condition, postulated in equation (2), to obtain a certain CO₂ capture efficiency value (E_{carb}) is that the active flow of CaO supplied to the carbonator is greater than the molar flow of CO₂ being captured when considering that value of E_{carb} .

$$F_{CO2}E_{carb} < F_{ca}(X_{ave} - X_{calc})$$
⁽²⁾

Equation (2) is plotted in Figure 3 with a minor rearrangement of terms. The variable of the x-axis, $F_{Ca}(X_{ave}-X_{calc})/F_{CO2}$, represents the active flow of CaO per mol of CO₂ entering the carbonator. The inclined line in Figure 3 represents the theoretical case where the two sides of equation (2) would be equal and hence the supply of active CaO and the CO₂ captured would be of stoichiometric proportion. Since most of the experimental points lie close to the solid line, equation (2) is adequately fulfilled. Points on the left of the line are in violation of equation (2) and can be explained based on the errors in the determination of the solid circulation flow and problems of representativeness of the solid samples analyzed. Experimental points having a E_{carb} value which deviates significantly from the equilibrium value, depicted in Figure 3 through the horizontal line, despite having an $F_{Ca}(X_{ave}-X_{calc})/F_{CO2}$ which is

greater than E_{eq} correspond to steady states where there is insufficient inventory in the carbonator or where gas-solid contacting limitations become significant, e.g. situations where large gas volumes bypass the carbonator bed. For the points where the $F_{Ca}(X_{ave}-X_{calc})/F_{CO2}$ is smaller than E_{eq} , the CO₂ capture efficiency is mainly limited from the quantity of active CaO flow entering the carbonator, as indicated from the inclined line. Such situations can occur due to low calcium looping ratio values (F_{Ca}/F_{CO2}), low X_{ave} and low calcination reaction efficiency and hence high X_{calc} values. This last term shows the importance of proper regenerator operation, although it is beyond the scope of this paper to discuss this in detail. In a large scale Ca-looping system there will always be a tradeoff between the need to achieve a X_{calc} value close to zero (full calcination) and the requirements of high temperatures and/or low partial pressures of CO₂ needed in the calciner to achieve such objective.

A further formulation of the carbon mass balance takes into account the CO_2 captured by the CaO in the bed.

$$F_{co2}E_{carb} = n_{Ca} \cdot \left(\frac{dX_{carb}}{dt}\right)_{reactor}$$
(3)

Where n_{Ca} is the mass inventory (number of mols) of Ca in the carbonator (mol) and $(dX_{carb}/dt)_{reactor}$ is the average reaction rate of these solids (s⁻¹), at average temperature and CO₂ concentration. This equation is the fundamental carbonator reactor design equation. In order to show the degree to which the experimental data of INCAR-CSIC and IFK fulfill the mass balance of equation (3), a number of aspects regarding the two right hand side terms have to be discussed first.

Axial carbonator pressure drop and CO₂ concentration profiles

The carbonator Ca solid inventory, n_{Ca} , is a variable of primary importance for carbonator operation, as shown by equation (3). When there are no other solids in the system, other than CaO or CaCO₃ (as is the case in the experiments at INCAR-CSIC and IFK), it can be estimated from the pressure drop measurements in the reactors and the carbonate content measured during the analysis of solid samples.

The carbonator riser solid loadings have been in the range of 200-500 kg/m² and 560-1170 kg/m² for the INCAR-CSIC and IFK case, respectively. This corresponds to a pressure drop between 2.0-4.9 kPa and 5.5-11.5 kPa for the INCAR-CSIC and IFK carbonator, respectively. The inventory distribution is not uniform, as indicated already in Figure 1. Due to this reason and based on that the carbonation reaction rate decreases as CO₂ is captured, the local CO₂ capture efficiency will vary with carbonator height as indicated by equation (3). In the case of IFK experiments, it has been possible to determine the axial pressure profile and axial CO₂ profile along the CFB carbonator, as shown in Figure 4. The distinct fluid-dynamic regions are demarcated by their different pressure drop gradients and solid fraction values (ε_s) . The lean core-annulus region, exhibits a pressure drop gradient of ca. 0.31 kPa/m corresponding to a solid fraction between 0.01-0.02. As is typical for this region the pressure drop gradient and therefore the solid fraction is higher at the bottom than at its top. In this region, solids move upwards from the center of the riser and downwards from the side. At the top of the riser, the exit region is observed, having an increased pressure drop gradient and solid fraction value approximately equal to 0.5 kPa/m and 0.03, respectively. This densification of the solid flow at the top of the riser is due to its abrupt riser exit. This fluid-dynamic region is typical for small scale risers and is absent in large scale systems, unless a significant constriction is applied to the flow. The dense region, located at the bottom of the riser exhibits the highest pressure drop gradients and solid fraction values. The dense region is contained within the first 3 m, as indicated by the corresponding measurement. The exact border of the dense region has not been obtained, since this would require a greater number of pressure measurements within this section. Assuming the typical solid fraction value of 0.2 for the dense region, its height is found equal to 1.2 m. Based on the same reasoning, the dense region height can reach values of above 2 m, when operating the riser with high solid loadings, i.e. > 1000 kg/m². As indicated by the axial CO₂ profile of Figure 4, the CO₂ vol.-% reduces from 11.40 % at the carbonator entry to 2.74 % at an axial riser height of only 0.73 m, i.e. within the dense bed region. When taking into account a total of 32 IFK steady states, conducted with axial CO₂ profile measurements, it can be noted that the CO₂ capture efficiency realized in the first 0.73 m of the dense region is always greater than 80 % of the total

carbonator CO₂ capture efficiency. Hence, it is clear that the dense region plays the biggest role in terms of CO₂ capture. However, the importance of the lean-core annulus and exit regions must not be underestimated. Taking into account the axial CO₂ profile of figure 4, it must be noted that the reduction of the CO₂ vol.-% from 2.5 % (measured at a riser height of 6 m) to 1.7 % (measured at the riser exit) corresponds to a CO₂ capture efficiency increase of 5.8 %, between these two axial heights. Therefore, the fluid-dynamic regions above the dense region can be considered as the polishing step in order to bring the CO₂ capture efficiency close to the equilibrium value, provided that there is enough active CaO in the reactor, as in the case of Figure 4. Furthermore, since the loop seals of the IFK facility and pressure measurement ports have been supplied with air, while the carbonator is fluidized with N2 and CO2, O2 is detected in the carbonator riser at small percentages, i.e. < 2%. The O2 vol.-% at the carbonator off-gas is higher than that measured at 6 m because of the mixing of the riser gas with air travelling up the standpipe. Additional reasons can be found in that pressure port purge air enters the riser at different axial points and that CO₂ capture is taking place between the height of 6 m and the riser exit. No O₂ is measured at 730 mm, since the loop seal return leg entrances come into the riser at axial heights of 1 and 1.2 m. Combining the above observations, which indicates that no gas back-mixing takes place, with the good match of the CO_2 profile with the pressure profile leads to the assumption that the carbonator riser can be considered as a plug-flow reactor for the gas.

Sorbent deactivation in the continuous DFB environment

The estimation of the reaction rate term of the design equation (3), uses experimentally determined values of the sorbent activity, X_{ave} , that are different for each sample. Through experimental derivation of the X_{ave} values, the difficulty of their estimation through a particle population balance in these small facilities is overcome. As experiments progress in time, there is a gradual drop in the average activity of the material due to particle deactivation, related to the increasing number of carbonation-calcination cycles that the average particle has experienced in the system. In future large scale facilities the average activity will not change with time due to the supply of fresh limestone, which is absent in the

experiments conducted here. Appropriate equations for the calculation of X_{ave} in such systems have been recently proposed^{11, 20}. The evolution of the X_{ave} during the course of long duration IFK and INCAR experiments is presented in Figure 5. The theoretical number of cycles (N_{th}) is plotted in the x-axis and is given in equation (4).

$$N_{th} = \int_{0}^{t} \frac{F_{CO2}E_{carb(t)}}{n_{Ca,total}X_{ave}} dt$$
(4)

Where $E_{carb}(t)$ represents the instantaneous CO₂ capture efficiency, while $n_{Ca,total}$ stands for the total inventory in the DFB system. Since the Xave is measured at different time points, its value is considered constant between these points. The product, $F_{CO2}E_{carb}(t)$, is calculated through gas analysis, while the total calcium moles are known through measurements of the initial bed inventory and of the solids extracted from the system at different time points. The Nth expresses the amount of times that the moles of CO₂ captured could carbonate the bed inventory (n_{Ca,total}) up to its average CO₂ carrying capacity (Xave). For a given theoretical cycle number, the INCAR-CSIC limestone samples exhibit slightly better average CO₂ carrying capacity than that of IFK. This can be attributed due to the better deactivation characteristics of the INCAR-CSIC limestone in comparison to that of IFK, as shown in Figure 2. Two further remarkable conclusions can be drawn from the same figure. The first is that it has been impossible in both installations to conduct experiments with highly active CaO, i.e. having a maximum carbonation conversion greater than 0.3 mol CaCO₃/mol Ca, as has been recorded during the TG experiments of Figure 2. Clearly, it is quite challenging to maintain the activity of the material during the first calcination of the limestone batch. This was already noted in experiments conducted in batch mode²¹ where it was speculated that the long times required for calcination of the initial limestone batch (hours) resulted in a higher effective carbonation/calcination number for the sorbent particles. The above speculation is reinforced, when considering that the residence times utilized for pre-calcination of the initial batch of solids were in the range of a few hours for both INCAR-CSIC and IFK. The second is that the residual activity attained by the solids as the theoretical cycle number increases, shown in Figure 5, is remarkably close to the one measured in the TG test of Figure 2. Hence, in both Figure 2 and Figure 5, the residual activity is around 0.1 and 0.07 mol CaCO₃/mol Ca for the INCAR-CSIC and IFK case, respectively. High values of CO₂ capture could be maintained also when operating with values of X_{ave} close to the residual activity provided that the calcium looping ratio (F_{Ca}/F_{CO2}) was such, in order to account for a product of $F_{Ca}/F_{CO2}X_{ave}$ approximately equal or greater than 1, as indicated in Figure 3. Finally, the positive deviation of the X_{ave} decay curve in the case of INCAR-CSIC, observed at a theoretical number of cycle of above 30, is attributed to the addition of 1 kg batches of fresh precalcined or used sorbent which has been recovered from the secondary cyclones, as a result of primary cyclone malfunctions described elsewhere¹⁷.

The characteristic parameter of active space time

As noted above, the carbonator profiles of Figure 4 lead to a plug-flow assumption for the gas-solid contacting model. This assumption is also supported by considering the turbulent nature of the flow in CFB operation mode, the long length of the risers and the relatively slow rate of the carbonation reaction. In order to be able to close the mass balance of equation (3) and to postulate a simple carbonator model two aspects have to be defined, i.e. (i) which percentage of the carbonator particles react with CO₂ and (ii) what is the appropriate expression of the reaction rate. The combination of these two aspects leads to the definition of the key carbonator parameter of active space time (τ_{active}), which has been shown to unlock a comprehensive design methodology²². Two approaches have been utilized in order to define this parameter and the aspects in question, namely approach A & B, both of which are given below. Letters A & B are used as subscripts to distinguish between symbols that are dependent on the type of the approach used and those that are not. In any case, it has to be noted that, for both approaches, the carbonation reaction is a first order reaction²³⁻²⁴ in respect to the logarithmic average concentration of CO₂, defined by the respective experimental inlet and outlet CO₂ concentration values.

a) Approach A assumes that the carbonator reactor operates with a bed, where all particles are able to react and have the same average characteristics. These include a carbonate content (X_{carb}) and the CO₂ carrying capacity (X_{ave}). The reaction rate of the particles and of the

whole carbonator bed has been considered proportional to the $(X_{ave}-X_{carb})$ difference, while the corresponding rate equation is given by equation (5) below.

$$\left(\frac{\mathrm{dX}}{\mathrm{dt}}\right)_{\mathrm{A}} = k_{\mathrm{sA}} \left(X_{\mathrm{ave}} - X_{\mathrm{carb}}\right) \left(\overline{v_{\mathrm{CO2}}} - v_{\mathrm{eq}}\right)$$
(5)

The above expression is consistent with experimental data on carbonation reaction rates reviewed by Bathia and Perlmuter²³ and more recently by Grasa et al.²⁴. As a result, taking into account the assumption that all the particles react with CO_2 and the rate expression of equation (5), equation (3) can be rewritten in the form given below after a minor rearrangement of terms.

$$E_{carb} = k_{sA} \, \varphi \, \tau \left(X_{ave} - X_{carb} \right) \left(\overline{\nu_{CO2}} - \nu_{eq} \right) \tag{6}$$

Where τ symbolizes the parameter of space time defined as the ratio of the moles of CaO present in the carbonator and the molar flow of CO₂ entering the reactor and φ is the gassolid contacting effectivity factor which has been defined elsewhere⁸. Based on equation (6), the parameter of active space time $\tau_{active,A}$ has been defined as the product of the space time and the reaction rate term of $(X_{ave}-X_{carb})^{8-9, 25}$, and is given in equation (7).

$$\tau_{\text{active},A} = \tau \left(X_{\text{ave}} - X_{\text{carb}} \right) \tag{7}$$

b) Approach B makes the assumption that only a fraction, f_{active}, of the particles of CaO with a sufficiently short residence time are active in the the bed and can react in the fast reaction regime²⁶. In addition, it postulates that the particles belonging to this fraction react with a reaction rate dependant on the limestone constant k_{sB}, the CO₂ carrying capacity X_{ave} and the difference of the actual and equilibrium CO₂ volume fraction. However, the reaction rate is taken to be irrespective of the particle carbonation conversion X_{carb}, until it equals X_{ave}. After this point, the reaction rate becomes equal to zero. The reaction rate expression described above is given in equation (8) for X_{carb} values lower than X_{ave}.

$$\left(\frac{dX}{dt}\right)_{B} = k_{sB}X_{ave}(\overline{v_{CO2}} - v_{eq})$$
(8)

The rate expression of equation (8) constitutes an oversimplification of the reaction rate model at particle level, but has shown to be consistent with some data series reported from TG studies²⁶. Figure 6 shows a plot of carbonation conversion against time of two samples that had been removed from the INCAR-CSIC and IFK facilities. It is shown, that the expression of equation (8) fits the TG curves well in both cases. However, the sample of INCAR-CSIC exhibits a prolonged transition period between the fast and the slow reaction regime, which can be explained based on that any analyzed sample is a mixture of particles with different individual X_N values. Furthermore, the method of derivation of the reaction constant k_{sB} and the X_{ave} is graphically shown in Figure 6. In the case of INCAR-CSIC the k_{sB} average value is equal to 0.33 s⁻¹, while in the case of IFK it equals 0.26 s⁻¹. The X_{ave} values of the INCAR-CSIC and IFK samples shown in Figure 6, are equal to approximately 0.16 and 0.10, respectively. These values are typical for most experiments carried out in this work, as shown in Figure 5. Since X_{carb} is too close to X_{ave} for a large number of samples, especially in the case of IFK, it is difficult or impossible in some cases to estimate a k_{sB} value from the original sample removed from the carbonator. Therefore, the samples in both cases are first calcined and then carbonated again in the TG in order to determine Xave. Moreover, the X_{ave} determined in this way will be slightly smaller to the value of the original sample because the natural trend of sorbent deactivation with increasing number of cycles. However, this difference can be ignored in this case due to the typically low values of Xave. Taking into consideration the assumption that only a fraction of the carbonator particles react in the fast reaction regime and the reaction rate expression of equation (8), equation (3) can be rearranged to the form of equation (9).

$$E_{carb} = k_{sB} \varphi f_{active} \tau X_{ave} (v_{CO2} - v_{eq})$$
(9)

The expression of equation (9) has the important advantage of facilitating a link between the average activity of the carbonator solids with their residence time distribution in the bed (see Alonso et al.²⁶ for a detail description of the model). This is because the fraction of active particles, f_{active} , reacting in the fast reaction regime corresponds to the fraction of particles with a residence time below a critical reaction time t*:

$$f_{active} = 1 - e^{\left(-\frac{t^{*}}{n_{Ca}/F_{Ca}}\right)}$$
(10)

Where t* is the time required for a sorbent particle, at the average concentration of CO_2 in the bed, to increase its carbonate content from X_{calc} to X_{ave} , after which the reaction rate becomes zero. The t* is given in equation (11) below

$$t^* = \frac{X_{ave} - X_{calc}}{(dX/dt)_{reactor}} = \frac{X_{ave} - X_{calc}}{k_{sB}\varphi X_{ave}(\overline{v_{CO2}} - v_{eq})}$$
(11)

Since, particles in the regenerator exhibit a residence time distribution, the X_{calc} of particles entering the regenerator will vary accordingly. However, in order to simplify this approach all particles entering the carbonator are considered to have the average value of X_{calc} measured experimentally. Based on the mass balance expression of equation (9) and equations (10, 11), the active space with use of this approach can be defined below:

$$\tau_{active,B} = f_{active} \tau X_{ave} \tag{12}$$

Where the product $f_{active}\tau$ is the space time of sorbent particles reacting in the fast reaction regime, while the X_{ave} is the key parameter defining their reaction rate.

Both equation (6) of approach A and equation (9) of approach B are carbonator reactor models that link directly or indirectly all calcium looping operating parameters with the CO_2 capture efficiency. The respective active space time expression is the key parameter of these models. It is indicative of both the sorbent inventory and the reaction rate of that inventory. For given carbonator reactor operating at given

fluidization conditions, limestone type, temperature and inlet CO_2 Vol.-% the active space time is the single parameter determining the CO_2 capture efficiency, as shown in equation (6) and equation (9).

Approach A has been used with relative success in previous fittings of carbonator reactor data. These data came from continuous carbonator systems exhibiting modest residence time values⁸⁻⁹, i.e. in the range of ca 1.5 min and batch experiments²¹. As noted, utilizing the active space time expression of equation (7) requires the experimental determination of the difference (X_{ave} - X_{carb}), for each experiment. This is obtained in TG experiments with samples extracted from the carbonator and assumed to be representative of the full bed inventory (see Rodríguez et al.⁸ for details). This approach has been demonstrated for both sets of continuous CFB carbonator data, i.e. those of INCAR-CSIC and IFK¹⁹. However, the application of this procedure to some of the IFK samples was found to be unacceptable because a large fraction of samples where giving very low values (even negative values) of the difference (Xave-Xcarb) despite coming from good experiments (with good closure of the carbon mass balances in the circulating solids). The IFK experimental data set shows very low values of (X_{ave}-X_{carb}) because of two reasons: the average CO₂ carrying capacity is consistently lower as explained above (Figure 5) and the solid bed inventories & average solid residence times in the reactor are larger in many experiments (see range of conditions in Table 1 which lead to an average IFK carbonator residence time of 3 min) leading to values of X_{carb} closer to X_{ave}. In contrast, the active space time expression of equation (7) fits the experimental data of INCAR-CSIC carbonator to a reasonable extent^{8, 19}. Therefore in the INCAR-CSIC case, the mass balance of equation (3) is fitted well when using the expression of equation (6).

For the IFK data set, approach B described above is clearly the best way to represent the data. This becomes apparent through the quality of the fit between the experimental data and the model expression of equation (9), which is presented in Figure 7. The y-axis and x-axis of this figure represent the left and right hand side of equation (9), respectively. Moreover, an equally good fit is achieved from the INCAR-

CSIC data. In addition, the apparent reaction rate constants ($k_{sB}\phi$) have been used as the fitting constant. Hence, the $k_{sB}\phi$ values derived were equal to 0.43 s⁻¹ and 0.20 s⁻¹ for INCAR-CSIC and IFK data sets, respectively. It has to be noted that for the INCAR-CSIC data, the fitted k_{sB} was found to be insensitive (sum of square error changes <5%) to changes of the apparent reaction rates between 0.30 and 0.60 s⁻¹. Since, most of the points are close to the 45° line in Figure 7, equation (9) is fulfilled to a satisfactory extent and the obtained fitting constants are considered valid. This adds significant confidence regarding the correctness of approach B and validates equation (9) as a simple yet efficient carbonator model. In addition, the gas-solid contacting factor φ is calculated for both installations, as the ratio of the apparent reaction rate constant ($k_{sB}\phi$) derived from fitting the experimental data to equation (9) and the reaction rate constant k_{sB} derived from the TG experiments, shown in Figure 6. The calculated value of φ is equal to 1.3 and 0.8 for the INCAR-CSIC and IFK case, respectively. At this point it has to be noted that φ is the effective fitting constant of the experimental data and model equation (9), since k_{sB} has been derived from the TG experimentation. As a result, the derivation of φ is burdened by the accumulation of the error of all measurements conducted during experimentation, i.e. gas, solid flow, temperature, pressure drop and TG measurements. Therefore, this justifies that the value of φ is slightly above 1 in the INCAR-CSIC case. However, what has to be pointed out is that both INCAR-CSIC and IFK φ values obtained are so close to 1 and that this is evidence of the excellent gas-solid contacting encountered in both CFB carbonator reactors. Moreover, this is despite the fact that the two carbonators are operating in different fluidization regimes, i.e. the turbulent and fast fluidization regime. Hence, both regimes can be considered for application in larger scale units. These neighboring regimes could be also combined in one carbonator unit. Hence, the carbonator can operate in the fast or the turbulent fluidization regime when original power plant is operating at full or partial load, respectively. However, the DFB design must be able to accommodate such a feature²⁷. In any case, the fact that the gas-solid effectivity factor (φ) has been derived close to 1 for both experimental installations enables the use of the mass balance expression of equation (9) as a simple carbonator reactor model. The only necessary

action before doing so is the determination of the reaction constant k_{sB} from a simple TG experiment, as shown in Figure 6, or in the absence of this information, the adoption of a k_{sB} value of around 0.3 s⁻¹.

Having acquired the k_{sB} and φ values needed for the calculation of $\tau_{active,B}$ as shown in equations (10-12), the equilibrium normalized CO₂ capture efficiency (E_{carb}/E_{eq}) is plotted against $\tau_{active,B}$, as shown in Figure 8. The active space time ($\tau_{active,B}$) correlates with the E_{carb}/E_{eq} well for both INCAR-CSIC and IFK data sets thus proving to be the characteristic carbonator parameter. In addition, the solid model lines obtained through equation (9) fit the experimental data to a satisfying extent. However, the solid model lines are different for the INCAR-CSIC and IFK case, firstly because of the different apparent reaction rate constant and secondly because most of the INCAR-CSIC experiments were conducted with an inlet CO₂ vol.-% of 16.5 %, considerably higher than the 11.4 % used in the IFK experiments. However, it must be noted that in the case of INCAR-CSIC only, approach A provides a marginally better fit of the experimental data. This means that the fit of the Ecarb/Eeq with the active space time expression of equation (7) of approach A¹⁹ is slightly better than with equation (12) of approach B, presented in Figure 8. Despite this fact, it is recognized that the approach B is more general, directly links the active fraction of the bed inventory with average residence time of the solids in the reactor and seems to give a reasonable quality fit for all data coming from both INCAR-CSIC and IFK installations. From Figure 8, a critical value of the engineering variable of active space time can be obtained, in order for the E_{carb}/E_{eq} to be greater than 0.9, which can be used to follow a carbonator design procedure²². This value is shown to be 30 s for the INCAR-CSIC case and 92 s for the IFK case. The difference, as noted, is mainly due to the different value of the fitted apparent reaction rate constant $(k_{sB}\phi)$ of the two systems and the difference between the inlet CO₂ Vol.-%. applied during experimentation. Furthermore, it has to be pointed out that the active space time values are rather close for both the INCAR-CSIC and IFK CFB carbonators despite further differences in operating conditions reported in Table 1. Moreover, they are close to the critical active space time value of 54 s, i.e. 0.015 h, reported when applying the fitting procedure described in approach A^{19} .

The carbonator reactor model of equation (9) and the active space time expression of equation (12), which have been validated by both INCAR-CSIC and IFK data sets, allow for both optimized design and operation of larger scale units. This has been the case in regard to the design of the next generation pilot scale systems, i.e. the 200 kWth DFB pilot²² already in operation at IFK, which has already demonstrated a CO₂ capture efficiency of 88 % under steady state conditions²⁷, and the 1.7 MW_{th} pilot located in La Pereda, Spain²⁸, which is under construction. However, the model of equation (9) can be further developed and the active space time expression of equation (12) can be further improved. For example, the effect of sulphation²⁹ and steam presence³⁰ on the reaction constant k_{sB} can be incorporated in the future. Moreover, the CO_2 adsorption taking place from the particle fraction (1-f_{active}), which is reacting in the diffusion regime, may also be taken into account thus obtaining a more "complete" form of equation (9) and a more accurate active space time expression than that of equation (12). The reaction rate of the diffusion regime in the vicinity of the Xave is generally two to three orders of magnitude lower than in the fast reaction regime (see for example Figure 6), but the average (1-factive) bed fraction can be one order of magnitude higer than the active fraction factive. Therefore, it can be claimed that the active space time has been slighly underestimated the previous analysis. Furthermore, a decisive development in regard to in depth carbonator modeling may come through the discretization of equation (9) and its application to different regions or cells of the reactor. Such an approach would require coupling of equation (9) with a semi-empirical¹¹ or more detailed CFD hydrodynamic model³¹⁻³². Such a model would allow the calculation of the local gas-solid effectivity factors thus improving model accuracy and allowing for the calculation of a global φ factor. Being able to estimate the global φ would allow a more objective assessment of the closure of equation (9) with use of experimental data, since no parameter would have to be used as a fitting factor. However, despite the simplifications which have been met in the derivation of the model expression of equation (9) and the active space time expression of equation (12), these equations have two striking advantages, i.e. they are simple to apply and fit the experimental data sets. Hence the equations and general results reported here can be used with greater confidence to

carry out first full simulations of the future industrial scale designs that will realize the postcombustion Ca looping concept at that scale.

CONCLUSIONS

The CFB carbonator reactor operating with a continuous flow of CaO is a key unit of the postcombustion Ca looping process and has been extensively characterized. This has been achieved with analysis of experimental data coming from two such reactors, located in INCAR-CSIC (Spain) and IFK (Germany). Despite variation in experimental conditions, the results proved comparable and allowed for extraction of common conclusions. Firstly, the closure of the carbon mass balances assured the quality of the results. Furthermore, it has been experimentally demonstrated that in order to capture a certain molar flow of CO₂, a slightly over-stoichiometric flow of active CaO is necessary. The solid flow structure of the CFB carbonator is shown to be of the dense bed, lean-core annulus and exit region type. The axial CO_2 profiles agree well with the solid flow structure, thus strengthening the assumption of plug-flow in regard to the gas phase. In addition, more than 80 % of the total CO₂ capture is shown to occur below the first meter of the carbonator riser, i.e. within the dense bed. The average CO_2 carrying capacity has been noted to decay with increasing theoretical cycle number for both installations due to deactivation. The experienced decay starts from values that are smaller than expected from TG tests and ends at values of residual activity close to those expected from these tests, i.e. 0.7-0.1 mol CaCO₃/mol Ca. Two approaches have been utilized in order to find a suitable expression for the characteristic parameter of active space time and provide a simple model for its correlation with the CO₂ capture efficiency. The first (approach A) assumed that all the particles in the carbonator bed react in the fast reaction regime and that their reaction rate is proportional to the difference between their average CO_2 carrying capacity (X_{ave}) and average carbonate content (X_{carb}). The second (approach B) assumed that a fraction of the particles react in the fast reaction regime which is dependent on a simple residence time distribution in the carbonator riser. Moreover, the reaction rate of this approach was considered to be proportional of the particles X_{ave} value only, provided that $(X_{carb} \le X_{ave})$ for a specific particle. 22

Approach A has shown to fit only INCAR-CSIC data well, while it has given unacceptable results for the IFK data sets. Main reason for this is the large residence time of solids in the IFK carbonator, leading to carbonate contents that are very close to the CO₂ carrying capacity of a particle. Approach B fits the data sets of both installations well and is considered more general, since it links the sorbent activity with a particle residence time distribution of particles in the carbonator. Depending on the inlet CO₂ concentration of the flue gas entering the carbonator, the active space time required in order for CO₂ capture efficiency higher than 90 % of the equilibrium value to be achieved is in the range of 30-92 s. The apparent reaction constants have been found to be equal to 0.43 s⁻¹ and 0.20 s⁻¹ for the INCAR-CSIC and IFK case, respectively. Therefore, the gas-solid contacting factor φ has been found to be in the range of 0.8-1.3 for both installations, thus demonstrating the excellent gas-solid contacting of the CFB carbonator reactor, independent of their operating regime, i.e. turbulent fluidization (INCAR-CSIC facility) and fast fluidization (IFK facility).

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NOTATION

 A_{carb} carbonator reactor cross section (m²) $(dX_{carb}/dt)_{reactor}$ reactor carbonation reaction rate (s⁻¹) E_{carb} CO_2 capture efficiency (-) E_{eq} equilibrium CO_2 capture efficiency (-)

$E_{\text{carb}}/E_{\text{eq}}$	equilibrium normalized CO ₂ capture efficiency (-)		
\mathbf{f}_{active}	fraction of active particles reacting in the fast reaction regime (-)		
F _{Ca}	calcium looping rate between reactors (mol/s)		
$\frac{F_{Ca}}{F_{CO2}}$	calcium looping ratio (-)		
F _{CO2}	CO ₂ flow to the carbonator (mol/s)		
F _{gas}	flue gas flow other than CO_2 (mol/s)		
Gs	riser entrainment (kg/m ² s)		
ks	surface carbonation rate constant (s^{-1})		
$k_{s}\phi$	apparent carbonation rate constant within the carbonator reactor (s^{-1})		
Ν	carbonation/calcination cycle number (-)		
N _{th}	theoretical number of cycle, realized within the DFB installation (-)		
n _{Ca}	amount of calcium in carbonator (mol)		
n _{Ca,total}	amount of calcium in the whole DFB system (mol)		
Р	carbonator pressure at a given axial height (Pa)		
t*	time needed for a particle entering the carbonator to increase it carbonate content		
	from X_{calc} to X_{ave} (s)		
T _{carb}	average carbonator temperature (°C)		
X _{ave}	average CO ₂ carrying capacity (mol CaCO ₃ /mol Ca)		
X _N	CO2 carrying capacity at carbonation/calcination cycle N (mol CaCO3/mol Ca)		

X _{calc}	average sorbent carbonate content in/after the regenerator (mol CaCO ₃ /mol Ca)			
X _{carb}	average sorbent carbonate content in/after the carbonator (mol CaCO ₃ /mol Ca)			
Greek letters				
ΔΧ	difference between X_{carb} and X_{calc} (mol CaCO ₃ /mol Ca)			
ε _s	solid fraction (-)			
ν_i	volume fraction of gas specie i (-)			
ν_{eq}	volume fraction of CO ₂ at equilibrium conditions (-)			
φ	gas-solid contacting effectivity factor (-)			
τ	carbonator space time (s)			
$ au_{active}$	active space time (s)			
Acronyms				
BFB	Bubbling Fluidized Bed			
DFB	Dual Fluidized Bed			
PSD	Particle Size Distribution			
TG	Thermo-Gravimetric			
Subscripts				
A	relates variables to approach A for active space time calculation			
В	relates variables to approach B for active space time calculation			

REFERENCES

(1) Anthony, E. J., Solid Looping Cycles: A New Technology for Coal Conversion. *Ind. Eng. Chem. Res.* 2008 (47) 1747.

(2) Blamey, J.; Anthony, E. J.; Wang, J.; Fennell, P. S., The calcium looping cycle for large-scale CO2 capture. *Progress Energy Combust. Sci.* 2010 (36) 260.

(3) Curran, G. P.; Fink, C. E.; Gorin, E., CO₂ acceptor gasification process. Studies of acceptor properties. *Adv. Chem. Ser.* 1967 (69) 141.

(4) Koppatz, S.; Pfeifer, C.; Rauch, R.; Hofbauer, H.; Marquard-Moellenstedt, T.; Specht, M., H₂ rich product gas by steam gasification of biomass with in situ CO₂ absorption in a dual fluidized bed system of 8 MW fuel input. *Fuel Process Technol.* 2009 (90) 914.

(5) Hawthorne, C.; Poboß, N.; Dieter, H.; Eder, T.; Holz, H.; Zieba, M.; Scheffknecht, G. *Pilot Plant Results of a 200 kWth Dual Fluidized Bed Gasifier Employing Adsorption Enhanced Reforming (AER)*.
3rd International Conference on Polygeneration Strategies, Vienna, 2011.

(6) Poboß, N.; Armbrust, N.; Zieba, M.; Scheffknecht, G. *Experimental investigation of affecting parameters on the gasification of biomass fuels in a 20kWth dual fluidized bed.* 3rd International Conference on Polygeneration Strategies, Vienna, 2011.

(7) Alonso, M.; Rodríguez, N.; González, B.; Grasa, G.; Murillo, R.; Abanades, J. C., Carbon dioxide capture from combustion flue gases with a calcium oxide chemical loop. Experimental results and process development. *International Journal of Greenhouse Gas Control.* 2010 (4) 167.

(8) Rodríguez, N.; Alonso, M.; Abanades, J. C., Experimental investigation of a circulating fluidizedbed reactor to capture CO2 with CaO. *AIChE J.* 2011 (57) 1356. (9) Charitos, A.; Hawthorne, C.; Bidwe, A. R.; Sivalingam, S.; Schuster, A.; Spliethoff, H.; Scheffknecht, G., Parametric investigation of the calcium looping process for CO2 capture in a 10 kWth dual fluidized bed. *International Journal of Greenhouse Gas Control*. 2010 (4(5)) 776.

(10) Charitos, A.; Hawthorne, C.; Bidwe, A. R.; Korovesis, L.; Schuster, A.; Scheffknecht, G.,
 Hydrodynamic analysis of a 10kWth Calcium Looping Dual Fluidized Bed for post-combustion CO₂
 capture. *Powder Technology*. 2010 (200) 117.

(11) Hawthorne, C.; Charitos, A.; Perez-Pulido, C. A.; Bing, Z.; Scheffknecht, G. *Design of a dual fluidised bed system for the post-combustion removal of CO₂ using CaO. Part I: CFB carbonator reactor model.* 9th International Conference on Circulating Fluidized Beds, Hamburg, 2008.

(12) Bi, H. T.; Grace, J. R., Flow regime diagrams for gas-solid fluidization and upward transport. *International Journal of Multiphase Flow.* 1995 (21) 1229.

(13) Rodriguez, N.; Alonso, M.; Grasa, G.; Abanades, J. C., Heat requirements in a calciner of CaCO₃ integrated in a CO₂ capture system using CaO. *Chem Eng J.* 2008 (138) 148.

(14) Abanades, J. C.; Grasa, G.; Alonso, M.; Rodriguez, N.; Anthony, E. J.; Romeo, L. M., Cost structure of a postcombustion CO₂ capture system using CaO. *Envrion Sci Technol.* 2007 (41) 5523.

(15) Löffler, G.; Kaiser, S.; Bosch, K.; Hofbauer, H., Hydrodynamics of a dual fluidized-bed gasifier-Part I: simulation of a riser with gas injection and diffuser. *Chem Eng Sci.* 2003 (58) 4197.

(16) Kronberger, B.; Lyngfelt, A.; Löffler, G.; Hofbauer, H., Design and Fluid Dynamic Analysis of a Bench-Scale Combustion System with CO2 Separation–Chemical-Looping Combustion. *Ind. Eng. Chem. Res.* 2005 (44) 546.

(17) González, B.; Alonso, M.; Abanades, J. C., Sorbent attrition in a carbonation/calcination pilot plant for capturing CO₂ from flue gases. *Fuel.* 2010 (89) 2918.

(18) Grasa, G. S.; Abanades, J. C.; Alonso, M.; Gonzalez, B., Reactivity of highly cycled particles of CaO in a carbonation/calcination loop. *Chem Eng J.* 2008 (137) 561.

(19) Rodríguez, N.; Alonso, M.; Abanades, J. C.; Charitos, A.; Hawthorne, C.; Scheffknecht, G.; Lu, D. Y.; Anthony, E. J. *Comparison of experimental results from three dual fluidized bed test facilities capturing CO₂ with CaO.* 10th International Conference on Greenhouse Gas Control Technologies (GHGT-10), Amsterdam, 2010.

(20) Rodríguez, N.; Alonso, M.; Abanades, J. C., Average activity of CaO particles in a calcium looping system. *Chem Eng J.* 2010 (156) 388.

(21) Abanades, J. C.; Anthony, E. J.; Lu, D. Y.; Salvador, C.; Alvarez, D., Capture of CO₂ from combustion gases in a fluidized bed of CaO. *AIChE J.* 2004 (50) 1614.

(22) Hawthorne, C.; Dieter, H.; Bidwe, A.; Schuster, A.; Scheffknecht, G.; Unterberger, S.; Käß, M. *CO₂ Capture with CaO in a 200 kWth Dual Fluidized Bed Pilot Plant*. 10th International Conference on Greenhouse Gas Control Technologies (GHGT-10), Amsterdam, 2010.

(23) Bhatia, S. K.; Perlmutter, D. D., Effect of the product layer on the kinetics of the CO₂-lime reaction. *AIChE J.* 1983 (29) 79.

(24) Grasa, G.; Murillo, R.; Alonso, M.; Abanades, J. C., Application of the random pore model to the carbonation cyclic reaction. *AIChE J*. 2009 (55) 1246.

(25) Abanades, J. C.; Alvarez, D., Conversion limits in the reaction of CO₂ with lime. *Energy Fuels*.2003 (17) 308.

(26) Alonso, M.; Rodríguez, N.; Grasa, G.; Abanades, J. C., Modelling of a fluidized bed carbonator reactor to capture CO₂ from a combustion flue gas. *Chem Eng Sci.* 2009 (64) 883.

(27) Hawthorne, C.; Dieter, H.; Holz, H.; Eder, T.; Zieba, M.; Scheffknecht, G. *High Temperature CO*₂ *Capture with CaO in a 200 kWth Dual Fluidized Bed Pilot Facility*. 2nd International Conference on Energy Process Engineering-Efficient Carbon Capture for Coal Power Plants, Frankfurt, 2011.

(28) Sanchez-Biezma, A.; Ballesteros, J. C.; Diaz, L.; de Zárraga, E.; Álvarez, F. J.; López, J.; Arias, B.; Grasa, G.; Abanades, J. C. *Postcombustion CO₂ capture with CaO. Status of the technology and next steps towards large scale demonstration*. 10th International Conference on Greenhouse Gas Control Technologies (GHGT-10), Amsterdam, 2010.

(29) Grasa, G. S.; Alonso, M.; Abanades, J. C., Sulfation of CaO Particles in a Carbonation/Calcination Loop to Capture CO₂. *Ind. Eng. Chem. Res.* 2008 (47) 1630.

(30) Manovic, V.; Anthony, E. J., Carbonation of CaO-Based Sorbents Enhanced by Steam Addition. *Ind. Eng. Chem. Res.* 2010 (49) 9105.

(31) Nikolopoulos, A.; Papafotiou, D.; Nikolopoulos, N.; Grammelis, P.; Kakaras, E., An advanced EMMS scheme for the prediction of drag coefficient under a 1.2 MWth CFBC isothermal flow--Part I: Numerical formulation. *Chem Eng Sci.* 2010 (65) 4080.

(32) Nikolopoulos, A.; Atsonios, K.; Nikolopoulos, N.; Grammelis, P.; Kakaras, E., An advanced EMMS scheme for the prediction of drag coefficient under a 1.2 MWth CFBC isothermal flow--Part II: Numerical implementation. *Chem Eng Sci.* 2010 (65) 4089.

		INCAR-CSIC	IFK			
General facility						
characteristics						
Limestone	-	Spanish	German			
		(98 % Ca)	(94 % Ca)			
Mean particle size	μm	130/180	170/350			
F _{Ca} /F _{CO2}	mol Ca/mol CO ₂	5-10	3-20			
Control of F _{Ca} /F _{CO2}		Fluidization of	Cone valve			
between reactors	-	riser, loop seal	Colle valve			
Carbonator						
characteristics						
Reactor type	-	CFB	CFB			
Height	m	6.5	12.4			
Diameter	m	0.10	0.07			
Gas velocity	m/s	1.1-3.5	4.0-6.0			
Thermal power	$\mathrm{kW}_{\mathrm{th}}$	30	10			
Fluidization regime	-	Turbulent	Fast			
Gs	kg/m ² s	1-4	10-20			
Inlet CO ₂ concentration	Vol%	0.03-0.25	11.4			
Temperature	°C	570-720	ca. 650			
Regenerator						
characteristics						
Reactor type		CFB	BFB			
Temperature	°C	850-900	ca. 900			
Partial Pressure of CO ₂	bar	< 0.3	< 0.3			
Particle residence time	min	1-5	1-5			
			Electrical heating			
		Electrical heating	& oxygen			
Method for heat supply	-	& air-fired coal	enriched air			
		combustion	(O ₂ =40 Vol %)			
			CH ₄ combustion			

Table 1. Main characteristics of the CFB carbonators of the INCAR-CSIC and IFK facilities.



Figure 1. Scheme of a continuous CFB carbonator reactor



Figure 2. Decay of the CO₂ carrying capacity, X_N, vs. the carbonation/calcination cycle number, N, for the Spanish limestone used by INCAR-CSIC and the German limestone used by IFK. (Carbonation conditions: 10% vol. CO₂ in air at 650°C; Calcination conditions: 10% vol. CO₂ in air at 950°C)



Figure 3. The CO₂ capture efficiency, E_{carb}, vs. the active flow of CaO circulating into the carbonator for all experimental runs.



Figure 4. Pressure profile, axial CO₂, O₂ profile for the IFK carbonator riser. Conditions: inlet CO₂ concentration 11.4 Vol.-% (rest N₂), O₂ source is air from the loop-seals entrances at 1 and 1.2 m, median particle size 340µm, superficial velocity 5.9 m/s, temperature 650°C, calcium looping ratio16.7, X_{ave} 0.065 mol CaCO₃/mol Ca, CO₂ capture efficiency 0.84 and equilibrium normalized CO₂ capture

efficiency 0.93



Figure 5. The decay of the average CO₂ carrying capacity (X_{ave}) with increasing theoretical cycle number (N_{th}). (Conditions: carbonator temperature 650 °C, inlet carbonator CO₂ vol.-% equal to 16.5 % (INCAR-CSIC) & 11.4 % (IFK), regenerator temperature 900 °C, regenerator residence time 1-5 min)



Figure 6. Carbonate content, X_{carb}, vs time and average CO₂ carrying capacity (X_{ave}) & reaction constant, k_{sB}, derivation for a calcined INCAR-CSIC and IFK sample removed from the CFB carbonators during operation. (Carbonation conditions: 10%-vol. CO₂ in air at 650°C)



Figure 7. Closure of the mass balance of eq. 9. Comparison of the CO₂ molar flow removed from gas phase with the CO₂ molar flow reacting with CaO in the bed of the carbonator reactor for all the experimental runs.



Figure 8. Normalized carbonation efficiency, E_{carb}/E_{eq} , vs. active space time, defined by eq. 12, for all the experimental runs. (Model lines conditions: carbonator temperature 650 °C, inlet carbonator CO₂ vol.-% equal to 16.5 % (INCAR-CSIC) & 11.4 % (IFK))