Comparison of experimental results from three dual fluidized bed test facilities capturing CO$_2$ with CaO

Nuria Rodríguez a *, Mónica Alonso a, Juan Carlos Abanades a, Alexander Charitos b, Craig Hawthorne b, Günter Scheffknecht b, Dennis Y. Lu c, Edward J. Anthony c

a INCAR-CSIC, Spanish Research Council, Francisco Pintado Fe, 26, Oviedo 33011, Spain
b IFK, University of Stuttgart, Pfaffenwaldring, 23, Stuttgart 70569, Germany
c Canmet Energy, Natural Resources Canada, 1 Haanel Drive, Ottawa, Ontario, Canada K1A 1M1

ABSTRACT
Postcombustion CO$_2$ capture technologies using CaO as a regenerable solid sorbent have emerged as a promising route to reduce electricity penalty and the cost of CO$_2$ capture from flue gases of both new and existing fossil fuelled power plants. Rapid progress is taking place in the understanding of these processes at different levels. However, experimental information, validating the concept under continuous operating conditions similar to those expected for large-scale application, remain scarce. We present here a comparative analysis of the results obtained in three laboratory-scale dual fluidized bed (DFB) test facilities in Spain, Germany and Canada. The test facilities range from 10 to 75 kWth with riser heights between 4.5 and 12.4 m. They have been operated to capture CO$_2$ with CaO from simulated flue gases in the bubbling, turbulent and fast fluidization fluid-dynamic regimes. The carbonator reactors are interconnected with regenerators, where the CaCO$_3$ decomposition has been conducted continuously and semi-continuously, operated in both air-combustion and oxy-combustion modes. Many stationary and non-stationary states have been achieved at different combinations of the key operating parameters (e.g. calcium looping ratio). All DFB test facilities showed a carbon balance closure of high quality in most tests. The trends of CO$_2$ capture efficiency with respect to operating conditions and sorbent characteristics are compared and a discussion is made on the most appropriate methodology to conduct future tests under a joint new FP7 project (CaOling) that aims at the rapid scaling up of the calcium looping technology.

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 Anthony [1] and Blamey et al. [2]). The process consists (Figure 1) 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 CaCO$_3$ formed. A CO$_2$-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 generate CaO and 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 cycling, operation mapping at different temperatures and pressures, reactivity towards CO2, SO2, etc.), sorbent improvement methods, reactor and process modelling, energy integration schemes and techno-economic studies of the full system. However, the experimental information validating the concept is still relatively recent and still 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-calculator operating at very high pressures and temperatures. Much more recently, rapid progress has been achieved also in the precombustion route. 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. Although these tests and experience 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 postcombustion applications are very different. In principle, the atmospheric conditions and low partial pressures of CO2 in a combustion flue gas, decreasing as CO2 is being captured in the reactor, make the effective adsorption of CO2 by CaO more challenging. However, an earlier set of experimental results obtained in a batch fluidized bed of CaO at the CANMET circulating fluidized bed (CFB) combustor pilot plant [5] proved that CO2 could be captured from flue gases at atmospheric pressure in a batch fluidized bed using reasonable gas residence times, bed inventories and reasonably active CaO derived from natural limestones by calcination. The recently published results of other batch tests carried out at laboratory scale in the same facility confirm the deactivation trends of sorbent and basic bubbling reactor modelling tools [6]. Lu et al. [7] reported stable capture conditions in a similar semi-continuous 75 kWth lab-scale DFB facility composed of an oxy-fired CFB calciner and a bubbling fluidized bed carbonator. Chartios et al. [8] have also performed continuous experimental tests on a 10 kW lab scale DFB composed of a bubbling fluidized bed (BFB) and a CFB, operated originally as the carbonator and the regenerator, respectively. They conducted a parametric study to define the link of main process operational variables and the carbonator CO2 capture efficiency. To achieve operational conditions closer to those expected in CFB reactors, Alonso et al. [9] and Rodriguez et al. [10] carried out experimental work in a 30 kW pilot plant composed of a CFB carbonator coupled with a CFB calciner. They reported CO2 capture efficiencies between 70 and 97% under realistic operation conditions in the CFB carbonator reactor. For the same reason that experimentation with use of a CFB carbonator is closer to industrial conditions the 10 kW IFK facility has been recently operated continuously utilizing its CFB as the carbonator and some conclusions are presented here. The focus of this communication is to present a comparative analysis of the methodologies and results obtained in the three laboratory-scale fluidized bed test facilities in Spain, Germany and Canada in regard to testing the postcombustion calcium looping concept. A joint discussion is also made on the most adequate methodology to conduct future tests under a joint new FP7 project (CaOLing) aimed at the rapid scaling up of this technology (see [11] in a different communication to this Conference).

Three calcium looping DFB electrically heated lab-scale facilities in the range of 10-75 kWth have reported successful operation of the process. These facilities are important tools for testing calcium looping parameters (e.g., calcium looping rate, solid inventory, effect of sulphur, etc.) and for sorbent
characterization. To further develop the process on a pilot scale, a 200 kWth DFB pilot plant has commenced operation at the University of Stuttgart and first experiences are reported in a separate publication within this conference [12], while a 1 MWth plant is expected to commence operation in 2011 in La Pereda, Spain.

CALCIUM LOOPING DUAL FLUIDIZED BED FACILITIES

General schemes of the three facilities considered in this work have been presented elsewhere. The INCAR-CSIC facility [9] consists of two circulating fluidized bed reactors: a carbonator and an air-fired regenerator. The height of the carbonator and the regenerator is 6.5 m and 6.0 m, respectively while both reactors have a 0.1 m internal diameter. The first 2.5 m of the risers and the loop seals are surrounded by electric ovens. The simulated flue gas, entering the carbonator, is synthetically pre-mixed and consists of air and carbon dioxide. The carbon dioxide reacts with active calcium oxide coming from the regenerator at temperatures between 600 and 700 °C. The formed calcium carbonate is regenerated in the CFB regenerator at temperatures between 800 and 900 °C. The mixture of gases and solids leaves the risers through the primary cyclones from where the solids fall through a vertical standpipe to bubbling fluidized bed loop seals. The loop seals are aerated with air and solids flow over them towards an inclined standpipe that directs them to the other reactor.

The IFK facility consists of a 12.4 m high, 70 mm diameter CFB and a 114 mm diameter BFB [8]. The BFB and the CFB can be optionally used as the carbonator or the calciner. Using the BFB as the carbonator allows reactor operation at low velocity conditions (< 1.2 m/s), while the BFB carbonator inventory remains unchanged with time due to the existence of an overflow. Using the CFB as the carbonator allows for a realistic assessment of a high-velocity carbonator operating at 4-6 m/s. Experimental results from both modes of operation are included in this communication. Reactors, standpipes and inlet gas streams are electrically heated. Carbonator and calciner temperature ranges are between 630-700 °C and 850-900°C, respectively. The carbonator inlet gas stream is a synthetic flue gas consisting of 11-15 %vol. CO2 and balance N2. Additionally, the regenerator is fired with natural gas when electrical heating is not sufficient to maintain the desired temperature. Loop seals are fluidized with air, thus allowing the quantification of loop seal gas entering the carbonator through O2 vol.% flue gas measurement. The novelty of this rig in comparison to other DFB systems is the control of the calcium looping rate between the beds by a cone valve located at the loop seal of the CFB. Solids enter the BFB through the cone valve and exit through an overflow located at its side and subsequently return to the CFB. Flue gases exiting from the CFB and BFB pass eventually through two cyclones and a candle filter to remove any remaining fines.

The CANMET dual fluidized mini-bed system can be broken down into two main mechanical systems and one solids transport system [6]. The first mechanical system is a calciner/regenerator that can be operated as a bubbling or a circulating fluidized bed combustor. The second mechanical system is a carbonator that can be operated as a bubbling or moving bed reactor. Finally, the solids transport system can be divided into the solids riser, transfer cyclone, and carbonator return leg. The calciner has a height of 4.5 m and the carbonator is 2 m tall. Each reactor has an internal diameter of 100 mm and is surrounded by three 4.5 kW electric heaters, which provide supplemental heating during start-up and can be switched on or off to control temperatures. The carbonated sorbent is calcined in the regenerator and returns back to the carbonator to repeat the cycle through a conveying line. The calciner is fluidized with oxygen-enhanced air and/or oxygen and recycled gas from a blower to control bed temperature. This is essential for the oxy-fuel process in order to achieve high concentration of CO2 in the exit gas from the calciner. Flue gas exits at the top of the calciner and is directed to the cyclone from where it passes through a heat exchanger for fine particle removal. In order to achieve solid transport, the solids from the regenerator bed are collected through a 45 degree “T” under the distributor. A solenoid valve controls the solid flow by conveying air through a 6.0 m conveying line so as to lift the solids up to the carbonator. This system allows collecting solid samples from the line and calculating
the sorbent cycle number based on the total amount of calcined sorbent in the system and the solid conveying line.

A first difference to consider among the three installations is that the operation of the CANMET pilot is in semi-continuous mode while the operation of IFK and INCAR-CSIC rigs can be in continuous circulation mode. During experiments at CANMET, for certain periods of time the whole mass of solids in the system is being carbonated while in other parts of the experiment the mass of carbonated solids is calcined. This is beneficial for data interpretation because the evolution of the number of cycles experienced by the solids in the system can be monitored. However, it makes it impossible to achieve steady state conditions in the reactors because the carbonation conversion of the solids in the reactors (and the fraction of active material in the bed reacting in fast carbonation regime) is changing with time. In contrast, data from INCAR-CSIC and IFK rigs can achieve stationary state conditions but at the expense of continuously mixing solids with different reaction histories and complicating the interpretation of results in terms of the evolution of the cycle number of the initial batch of solids. Furthermore, differences exist in the manner of conducting both carbonation and calcination. The carbonators of the three facilities provide different gas-solid contacting modes which influence reactor performance and are dependent on reactor type (CFB or BFB), superficial velocity and particle size. These include the moving bed regime (CANMET), the bubbling fluidized bed regime (CANMET & IFK), the turbulent regime (INCAR-CSIC) and the fast fluidization regime (IFK). Calciner operation is different among the three facilities in terms of fuel type used and calcination atmosphere. The most realistic conditions are those of oxy-fuel calcination with solid fuel use and have been realized by CANMET. On the other hand INCAR-CSIC operates its calciner through air combustion of solid fuels, while IFK uses natural gas under air or oxygen enriched air conditions (O₂ %vol. up to 40%). A further difference is associated with experimental procedure, i.e., the way of measuring the looping rate between the reactors. INCAR-CSIC performs this by directing the solid flow to a dead volume for a given period of time and weighing the collected solids, while IFK measures the particle bed height of accumulating solids in a quartz glass standpipe segment, once the aeration of the loop seal connecting the calciner and the carbonator has been shut off. Finally, the three rigs have used different limestones for performing experimentation. CANMET has used limestone with a median particle size of 400–800 μm. INCAR-CSIC has carried out experiments using two different limestones that presented very similar chemical behaviors with an average particle size around 130-180 μm [13]. IFK has used only local limestones and experimental results reported here correspond only to a German limestone, called Swabian Alb A with a median particle size of 350 μm and its chemical composition has been reported elsewhere [8].

The three installations are able to report reliable CO₂ capture efficiencies as the CO₂ disappearing from the gas phase is calculated by the inlet and outlet CO₂ concentrations. It is not the subject of the present communication to reproduce the data on CO₂ capture efficiencies presented by the authors elsewhere[7-9]. The series of experiments conducted with use of the different facilities proved that they are capable of achieving high CO₂ capture efficiencies, above 70%, over a wide range of operating conditions. However, an example of CO₂ capture efficiency measurements over time from each facility is included here and they are shown in Figure 2, with operating conditions included in the legend. Despite similar carbonator temperatures and space times, the CO₂ capture efficiency obtained in the IFK facility is higher than that of INCAR-CSIC. This is primarily attributed to the much larger molar calcium looping ratio of the IFK
carbonator ($F_{\text{CaO}}/F_{\text{CO}_2}=18$) compared to the INCAR-CSIC unit ($F_{\text{CaO}}/F_{\text{CO}_2}=8$). A further reason is that the INCAR-CSIC sorbent utilized in the experiment of Figure 2 is very sintered, having a maximum carbonation conversion ($X_{\text{max}}$) of only 8%. Both of the above aspects lead to more active sorbent per $CO_2$ flow in the IFK carbonator and therefore higher $CO_2$ capture efficiency. On the other hand, the very good gas-solid contacting of the INCAR-CSIC CFB carbonator results in obtaining a high $CO_2$ capture efficiency (above 70%) with a modest molar ratio of $F_{\text{CaO}}/F_{\text{CO}_2}$ (approximately equal to 8), which has been considered for steam cycle study [14]. Additionally, the fact that the $X_{\text{max}}$ in the case of INCAR-CSIC is only 8% leads to the conclusion that it is possible to operate an industrial Calcium Looping system, also with minimal make-up flow. A carbonation test of a CaO batch of around 7 kg carried out at CANMET facility is also shown in Figure 2. High $CO_2$ capture efficiency is achieved once the operation conditions are satisfied with thermal equilibrium. The dashed line in Figure 2 represents the average carbonation efficiency limit imposed by the equilibrium at the median operation conditions of the experiments. It generally can be stated, based on the combined operational experience that high $CO_2$ capture efficiencies are obtained when there is sufficient active CaO in the carbonator per incoming $CO_2$ flow and this is ensured by a combination of operational parameters. These include the circulation of CaO between the reactors, carbonator inventory and sorbent make-up flow to maintain sorbent activity.

The methodology to interpret experimental results is similar in the three rigs. The experimental information is first internally validated in all installations with the closure of a carbon mass balance. At INCAR-CSIC and IFK, the independent measurements of solid circulation rate and the difference in carbonation conversion between carbonator and calciner ($\Delta X$) allows for an adequate closure of the carbon mass balance ($CO_2$ disappeared in the carbonator = $CaCO_3$ circulating between reactors). The closure of the carbon mass balance is represented in Figure 3. The data points of the experiments conducted with a BFB carbonator at IFK are approximately on the $45^\circ$ line. On the other hand, experiments conducted with use of a CFB carbonator at IFK and INCAR-CSIC exhibit slight deviation. This can be explained, due to the larger circulation rates between the beds required when conducting carbonation in a CFB and the associated difficulties of measuring them with existing methods. As can be seen in Figure 3, some

![Figure 2. Example of experimental capture efficiencies ($E_{\text{carb}}$) in the three rigs for different conditions and reactors set-ups. ($T_{\text{carb}}$: average carbonation temperature; $u_g$: average gas velocity; $N_{\text{CaO}}/F_{\text{CO}_2}$: space time; $F_{\text{CaO}}/F_{\text{CO}_2}$: calcium looping ratio between reactors; $v_{\text{CO}_2}$: $CO_2$ inlet volume fraction)
experiments in CFB carbonators have achieved high CO₂ throughputs, closer to what is expected for large-scale application of the carbonator reactor, i.e. > 6 mol/m²s.

![Figure 3. Experimental comparison between the CO2 removed from the gas (mol/m²s) in the carbonator and the CaCO₃ formed (mol/m²s) in the solid circulating stream for INCAR-CSIC and IFK facilities. (Xcarb: carbonation conversion; FCaO: calcium molar flow circulating between reactors. FCO₂: molar flow of CO2 in the flue gas feed; Ecarb: capture efficiency in the carbonator).](image)

A second formulation of the CO₂ mass balance takes account of the actual reaction process of CO₂ with the CaO in the bed, and can be expressed as:

\[
F_{\text{CO}_2} \cdot E_{\text{carb}} = N_{\text{CaO}} \cdot X_{\text{active}} \cdot \frac{dX_{\text{carb}}}{dt}\bigg|_{\text{reactor}}
\]  

This is actually the fundamental design equation of the carbonator reactor and is, therefore, most interesting for scaling-up purposes. \(N_{\text{CaO}}\) is the mass inventory (number of mols) of CaO in the carbonator (mol/m²), \(X_{\text{active}}\) is the active fraction of CaO that is reacting in the fast reaction regime and \(dX_{\text{carb}}/dt\bigg|_{\text{reactor}}\) is the average reaction rate of these solids in the reactor (s⁻¹) at the average temperature and average CO₂ concentration in the carbonator. When there are no other solids in the system than CaO or CaCO₃ (as is the case in most experiments at INCAR-CSIC, IFK and CANMET), the bed inventory of solids can be estimated from the pressure drop measurements in the reactors and the carbonate content measured during the analysis of solid samples. This direct measurement of the bed inventory in the reactor and the outlet CO₂ gas concentration avoids the need for a hydrodynamic model to estimate this critical parameter in this particular experimental set-up. Future models of the reactor aimed at scaling up will have to incorporate such a hydrodynamic sub-model to estimate this inventory as a function of operating conditions, solid characteristics and bed geometry and this is well advanced in some of our groups [15, 16].

In order to estimate the reaction rate term of equation (1), we assume that the bed contains, besides the fraction of active CaO reacting in fast regime (\(X_{\text{active}}\)), a fraction of inactive CaO from previous carbonation/calcination cycles, and a fraction of CaCO₃ resulting from the carbonation conversion (\(X_{\text{carb}}\)). Under these conditions, the reaction rate term can be estimated from independent kinetic data, provided that the fraction of active CaO in the bed inventory of solids and the average concentration of CO₂ in the gas phase are known. Assuming a first order carbonation reaction rate and knowing from sample analysis the relevant carbonate conversions and hence the value of \(X_{\text{active}}\), it is possible to analyse the main trend of CO₂ capture efficiencies with some key operating variables [8, 10].
Grouping the main variables that affect the carbonation efficiency, the active space time ($\tau_a$) is defined as the ratio of active moles of CaO in the bed inventory ($N_{CaO} \cdot X_{active}$) and the molar flow of CO$_2$ in the flue gas feed ($F_{CO2}$). The active space time expresses the carbonator inventory active to react in the fast reaction regime for a given CO$_2$ flow. Following this definition, equation (1) is rewritten as follows:

$$E_{carb} = \tau_a \cdot \frac{dX_{carb}}{dt}_{reactor}$$

Figure 4 shows the trend of equilibrium normalized CO$_2$ capture efficiency as function of the active space time ($\tau_a$) for INCAR-CSIC and IFK data obtained over a range of conditions (about $T_{carb}=634-660$ °C, $v_{CO2}=0.11-0.17$, $X_{max} = 0.08-0.23$). The normalization of the capture efficiency with respect to the maximum permitted by equilibrium removes the effects of temperature and inlet CO$_2$ concentration on absolute capture efficiency. The trend line indicates that a sufficient amount of active inventory is required in the carbonator in order to achieve high CO$_2$ capture efficiencies. The trend line given by equation (2) fits the data from the INCAR-CISC and IFK test rigs when both are using a CFB as the carbonator. Since equation (2) does not account for reactor hydrodynamics, it can be concluded that there is excellent gas-solid contacting in the CFB carbonator which operate in the turbulent or fast-fluidization regimes. However, the situation is much different when comparing data produced from IFK’s BFB carbonator to the CFB carbonators. For the given conditions, the IFK BFB carbonator exhibits a much lower CO$_2$ capture efficiency at the same active space time compared to the INCAR-CSIC and IFK CFB carbonators. This is not surprising since BFB hydrodynamic models as well as cold model experimentation signify that a portion of the flue gas does not come in contact with the solids, but passes through the bed in a bubble phase, which is likely the case in the IFK BFB carbonator. To account for poorer contacting, the trend line of the IFK BFB carbonator data is fitted as a Mixed Flow Reactor. Regardless of the fluid-dynamic regime of operation, hydrodynamic-kinetic models as shown in [15], are required in order to improve the carbonator design and optimize CO$_2$ capture. Finally, a critical active space time value, defined in [8], exists for both contacting modes, i.e., BFB and CFB, above which the CO$_2$ capture efficiency approaches equilibrium values ($E_{carb}/E_{eq}>90\%$). This value is 0.05 h for the IFK BFB carbonator and approximately 0.015 h for the INCAR-CSIC and IFK CFB carbonators.

![Figure 4](image_url)
Experimental data from three different dual bed facilities with different configuration, detailed designs and modes of operation and fluidization regimes have confirmed the technical viability of high-temperature calcium looping systems for postcombustion CO$_2$ capture applications. Closure of carbon balances between reactors is shown to be satisfactory for all rigs. When a certain space time (0.015 h for INCAR-CSIC and IFK CFB carbonators and 0.05 h for IFK BFB carbonator) is reached in the bed, CO$_2$ capture efficiencies can go over 90%, close to the maximum allowed by the equilibrium of CO$_2$ on CaO. Lower CO$_2$ capture efficiencies, between 50-80%, are obtained when the solid inventory of active material decreases by deactivation of the sorbent, extensive carbonation of the bed material and/or, insufficient total inventory of solids in the riser. A simple model that accounts for the decay in sorbent CO$_2$ capture capacity and the carbonation reaction rate expected in the well mixed materials present at any point in the carbonator reactor is able to provide a common interpretation of all results. It has been demonstrated that the effect of operating parameters such as temperature, gas velocity and solid circulation rate can be understood through the link of these variables with the inventory of active CaO in the riser. The overall conclusion from this analysis is that, despite the differences encountered in some particular results and the limitations of our individual units, the CaO looping process has shown good consistency between the different facilities operating in a similar hydrodynamic fluidization regime. Furthermore, the range of operating conditions resulting in high capture efficiencies demonstrate that calcium looping can become a major technology option for CO$_2$ capture in the medium term.

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REFERENCES


