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Calcium Looping Process: Experimental investigation of limestone performance regenerated under high CO_2 partial pressure and validation of a carbonator model.

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Abstract

A key aspect of the Calcium Looping process is the implementation of the oxy-fuel combustion for the endothermic sorbent regeneration, which imposes high partial pressure of CO_2 (75vol.-% dry). These conditions enhance lime sintering and thus, the decrease of the sorbent's maximum CO_2 carbonation conversion (X_{max}), which is an important parameter that influences the CO_2 capture. This paper presents results from tests performed in presence of high CO_2 volumetric concentration in a $10kW_{th}$ Dual Fluidized Bed system. High regeneration extents and CO_2 capture efficiencies of more than 80% is attained with sorbent residual activity of 8,5%. A carbonator model is validated and active space time is proposed to be the main parameter to be used for up scaling design purposes.

1. Introduction

Climate change requires the reduction of CO_2 emissions originating from coal combustion a major and stabilizing factor in the world electricity generation for the next decades. The use of new technologies is focused on the improvement of the efficiency of the existing coal fired power plants or the construction of new generation high efficiency ones or IGCC plants, the co-firing of CO_2-neutral fuels i.e biomass, the replacement of hydrocarbon fuels with renewable resources as well as the CO_2 capture and storage (CCS) in order to achieve the targets of reducing greenhouse gas emissions. Commercial CO_2 sequestration

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technologies can be divided into combustion in O_2 instead of air (oxy-fuel combustion), production of a carbon free fuel (pre-combustion) and separation of CO_2 from flue gas (post-combustion) including the Calcium Looping Process, which is the focus of this paper.

The calcium looping process already industrially used for syngas CO_2 removal from the 1960s [1] was firstly proposed by Heesink and Temmink in 1994 [2] as one of the Zero Emission Coal Technologies. The separation of the CO_2 is done in a dual fluidized bed system by means of the exothermic carbonation reaction of lime CaO so that $CaCO_3$ is formed while the regeneration of the CaO makes use of the endothermic calcination reaction (1). The second one is carried out in the regenerator, where coal is burnt under oxy-combustion conditions to drive the high temperature calcination process as proposed by Shimizu et al. [3]. The O_2/CO_2 combustion process provides an additional advantage and makes the technology competitive [4, 5, 6, 7]. Results from the IFK 10kW$_{th}$ and the CSIC 30kW$_{th}$ Dual fluidized Bed bench scale facilities [8, 9] as well as from the IFK 200kW$_{th}$ [10, 11], the TU Darmstadt 1MWth [12] and the La-PeredaCO$_2$ 1MW$_{th}$ [13] pilot plant tests confirm the feasibility of the concept and provide data for the process commercialization.

$$CaO_{(s)} + CO_{2(g)} \Leftrightarrow CaCO_{3(s)} \qquad\qquad \Delta H_{25°C} = \pm178.2 \text{ kJ/mol} \qquad\qquad (1)$$

The oxy-combustion of a fuel in the calciner implies high CO_2 concentration in the off-gas (around 85 vol.-% dry basis) and requires a flue gas recycle in the range of 50-60%. Therefore, this is the environment where the regeneration of the sorbent takes place. In this high CO_2 concentration atmosphere the loss of the carbonation capacity due to sintering [14] is one of the major concerns for the process drawback. Experiments performed at a 75kW$_{th}$ plant showed that the oxy-combustion of a solid fuel for sorbent regeneration in a CFB reactor allows for a good performance of the CaL process [15]. Recently the kinetics of the calcination reaction was studied in a Thermogravimetric Analyser by Martinez et al. [16], and it has been found that temperatures around 900°C are enough to achieve complete calcination under CO_2 concentrations and residence times typical in CaL.

In this frame, the goal of this work is to examine the effect that the high partial pressure of CO_2 has on the sorbent performance in realistic process conditions for the calcium looping process (residence time, temperature, CO_2 partial pressure). For this purpose, the experiments were carried out in the 10 kW$_{th}$ Dual Fluidized Bed facility. The results of this study are compared to those obtained by Charitos et al. [8, 9] for the regeneration under lower partial CO_2 pressure. Moreover, the carbonator model and the characteristic design parameter of active space time proposed in [9, 17] for the partially oxy-fired sorbent regeneration is further validated.

2. Experimental

Fig. 1. The 10 kW$_{th}$ IFK Dual Fluidized Bed Facility

Legend
1. Riser-CFB
2. Cyclones
3. Candle Filters
4. Upper Loop Seal
5. Cone Valve
6. BFB
7. Middle Loop Seal
8. Electrical Heaters

The experiments were carried out with a limestone originating from South Germany which has a great potential to be commercially used when process up-scaling. This limestone is mechanically quite stable in terms of attrition losses but chemically is quite poor in terms of carbonation conversion [18]. The chemical composition of this limestone as well as its particle size distribution is shown in table1a and b below and was determined with use of an XRF spectrometer and a vibrator sieve shaker.

Table 1a. Limestone chemical composition (wt.%)

CaO	SiO$_2$	Al$_2$O$_3$	MgO	Fe$_2$O$_3$	K$_2$O	Na$_2$O	TiO$_2$
53,64	3,506	0,50	0,51	0,18	0,08	0,02	0,02

Table 1b. Limestone particle size distribution

0-90 mm	90-250mm	250-500mm	500-710mm
8,1%	11,5%	71,6%	8,8%

Experiments were performed in the IFK 10kW$_{th}$ facility described elsewhere [8]. A new concept was implemented here, including a bottom loop seal, as shown in Fig. 1, in order to increase the flexibility in the reactor mass load and thus, the solids residence time. The experimental procedure was as follows.

Fresh limestone was initially fed to the system, which was electrically heated up to 700 °C in the regenerator and 600 °C in the carbonator. When these temperatures were reached, CH_4 was burned to ensure a fast heating up to the wished calcination temperature of 900 °C. During regeneration the bed was fluidized with air, O_2 and a CO_2 stream whereas the carbonator and the loop seal were fluidized with N_2. A stream of 13.5 vol.-% CO_2 (dry basis) was fed to the carbonator to simulate the real flue gas from a power plant. SO_2 was not present during the experiments for the sake of simplicity. The regeneration took place in an atmosphere containing 5 vol.-% steam, which was produced by the CH_4 combustion. The carbonator and the regenerator operated under the fast and turbulent fluidization regime respectively. The experimental parameters are summarized in table 2 below.

The regenerator efficiency is determined as the ratio of the carbonate content of the sorbent that is calcined to the one that can be calcined (equ. 2). X_{carb} and X_{calc} is the carbonate content of the sorbent respectively entering and exiting the reactor. The carbonator efficiency or CO_2 capture efficiency (E_{CO2}) is calculated on a molar flow basis through the experimental data provided by the gas analyzer and the gas flow measurements (equ.3).

$$n_{reg} = (X_{carb} - X_{calc}) / X_{carb} \tag{2}$$

$$E_{CO2} = (F_{CO2in} - F_{CO2out}) / F_{CO2in} \tag{3}$$

Table 2. Operational conditions of the carbonator and the regenerator

Parameter	Carbonator	Regenerator
Temperature (°C)	630	900
Fluidization velocity (m/s)	4.0-5.0	1.2-2.0
CO_2 concentration (vol.-%)	13.5 (in)	45-55 (out)
Bed pressure (mbar)	50-100	60-80
X_{max} (%)	8.5-21.5	-
$X_{carb/calc}$ (%)	7.8-21.9 (carb)	0.7-3.2 (calc)
Active Space Time (s)	10 - 50	-
Efficiency	0.4-0.85	0.82-0.98

The data presented here were collected at the end of steady state periods (fig.2), which are defined as those where the pressures, the temperatures, the outlet gas concentrations as well as the recirculation rates remain constant for a period of at least 15 minutes. Fresh limestone was added to the system from time to time to overlap the losses due to attrition and the possible cyclone inefficiency. The circulation rates were measured manually through a by-pass pipe specially designed for this purpose. Samples were collected after each steady state from both the regenerator and the carbonator outlet. A thermo-gravimetric analysis was carried out for each sample to define the carbonate content as well as the maximum carbonation conversion (X_{max}), which is the amount of CO_2 that can be up-taken in the fast carbonation regime. The analysis was performed in an innovative TG Analyzer developed by the IFK in cooperation with the company Linseis Thermal Analysis.
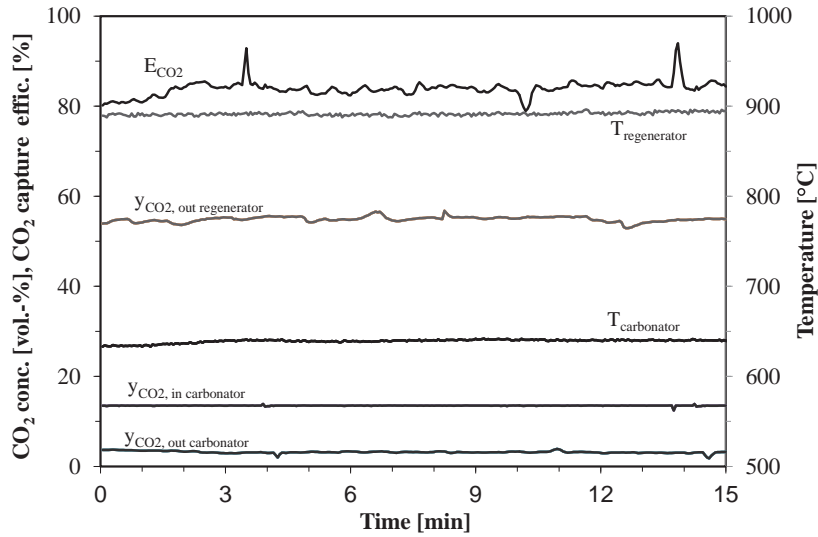
Fig.2.Example of a steady state

The validation of the experimental data was carried out by means of the simple carbon mass balance given by Equ.4. The closure of the carbon mass balance takes into consideration that the CO_2 captured in the carbonator is released in the regenerator plotted (Fig.3.). The experimental points obtained for low CO_2 vol. concentration during regeneration [9] are hereto presented as a base case useful for comparison reasons. As can be seen the mass balance closes quite well while small deviations are due to experimental errors during sampling, analysis as well as measurement of the circulation rates.

$$E_{carb} \cdot F_{CO2} = F_{ca} \cdot (X_{carb} - X_{calc}) \tag{4}$$
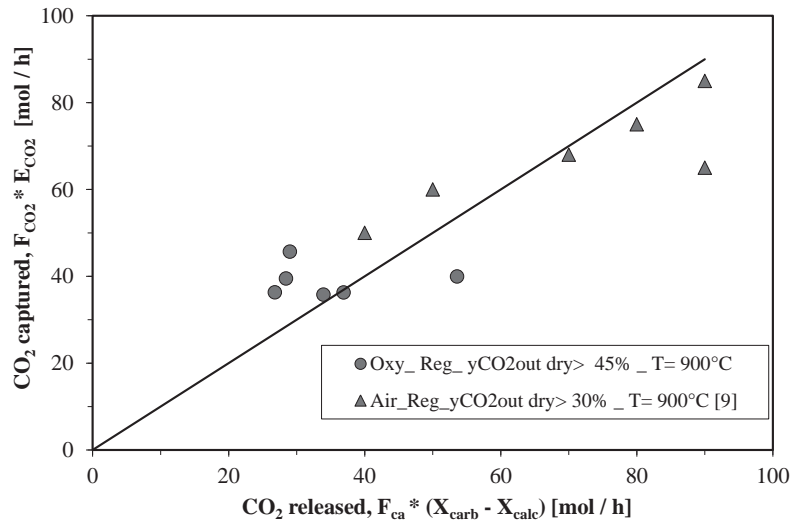
Fig.3. Mass balance closure

3. Results –Discussion

The efficiency of the carbonator is recently expressed [9] by equ. 5 below. From the expression it is obvious that the parameters affecting the efficiency are the kinetic constant K_s (dependent on the limestone), the gas solid contact factor (φ) (dependent on the reactor), and the volumetric concentration of the CO_2 in the power plant flue gases (V_{CO2}) and the equilibrium CO_2 volumetric concentration V_{equil}.

$$E_{CO2} = K_s \cdot \varphi \cdot \tau_{active} \cdot (V_{CO2} - V_{equil}) \tag{5}$$

The term of Active Space Time (τ_{active}) included in the equ. 5 above expresses the active flow (f_{active}) of the total available limestone (n_{ca}) for a certain CO_2 molar flow (F_{CO2}), namely space time, τ (equ.6) with a carbonation content available to react in the fast reaction regime (X_{max}), as per equ.3 below.

$$\tau_{active} = f_{active} \cdot \tau \cdot X_{max} \tag{6}$$

$$\tau = n_{ca} / F_{CO2} \tag{7}$$

Active flow of the limestone (f_{active}) is the one which react in the fast reaction regime as per (8) below. t* is the time needed for the sorbent to achieve the X_{max}.

$$f_{active} = 1 - exp(-t*/(n_{ca}/F_{CO2})) \tag{8}$$

The Active Space Time has been previously proposed as the main process design parameter [9]. Fig. 4 depicts the CO_2 capture efficiency versus the Active Space Time. The experimental data trendline fit well to the experimental data trendline as per [9]. It can be derived that for a certain sorbent CO_2 carrying capacity, a certain residence time and a molar flow of CO_2 to be captured, certain carbonator efficiency can be achieved. An active space time of 50s is required for high CO_2 capture efficiencies similar to the one proposed by the literature.
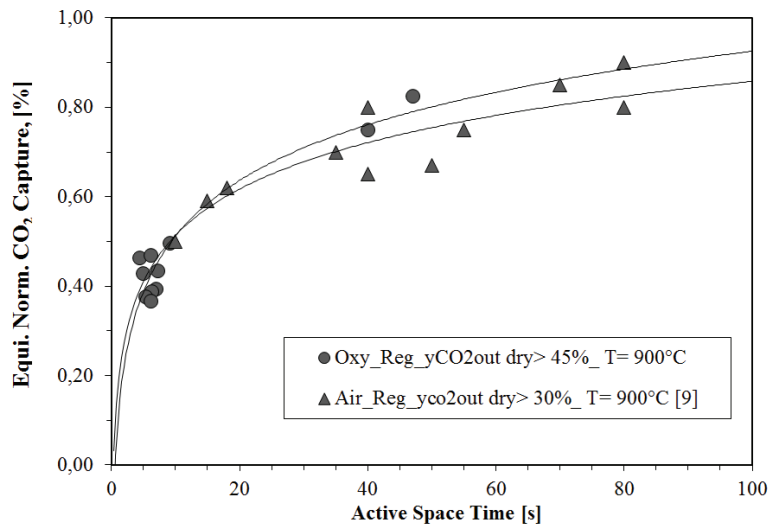

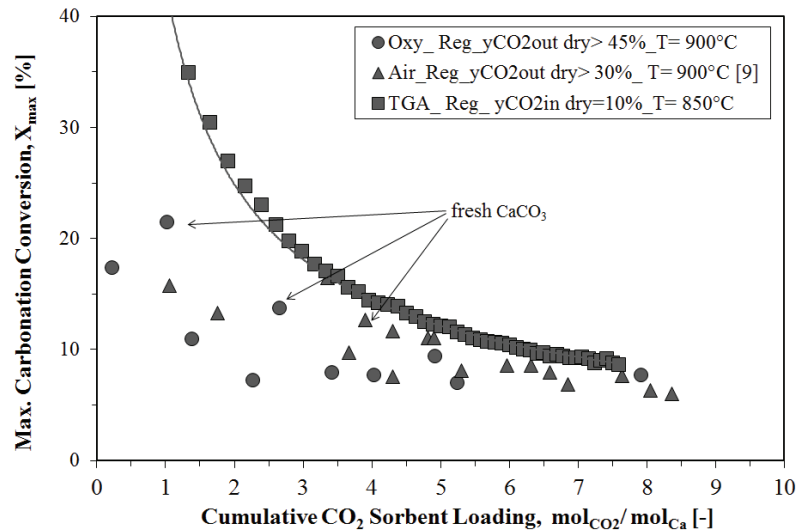Fig.4 Equilibrium normalized CO_2 capture efficiency vs Active Space Time

Fig.5 Decay of the maximum carbonation conversion vs the cumulative CO_2 sorbent loading

A second characteristic parameter related to the sorbent properties is the CO_2 carrying capacity. It is well known from TGA experiments that the carbonation conversion of limestone decays rapidly with the time and the carbonation-calcination cycle number [19, 20]. The cumulative sorbent loading of CO_2 is the parameter used to compare the decay of the limestone CO_2 carrying capacity for experiments carried out at the thermo gravimetric analyzer to those from the bench scale dual fluidized bed facility. This parameter expresses the total amount of CO_2 that the particle has captured during its lifetime. From the figure above it is identified that the limestone carrying capacity decays rapidly and achieves a residual activity of approx. 8,5%. It can be noticed that the same values are reported in the literature for low CO_2 partial pressures [8]. For low sorbent loading the theoretical TGA curve deviates from the results obtained in the fluidized bed, which is reasonable taking into consideration the fluidizing phenomena in the bed. In the fluidized bed the sorbent is imposed to severe thermal and mechanical stresses that change the surface and the pore structure and thus the maximum carbonation conversion. The sorbent achieves its residual activity and this is independent of the partial pressure of CO_2 during regeneration. The partial pressure of CO_2 seems to accelerate the decay of the carbonation conversion which is in agreement with the literature [21]. For technical reasons the surface area and the pore volume of the samples are not included in this work. It should be noticed that the results from the literature [8] depict a limestone that was pre-calcined for many hours and afterwards was used for the simulated air-fired case experiments. This fact sintered highly the limestone and this was observed through a loss in the BET surface area and a decrease in the pore volume. Finally, it must be noticed that in large scale facilities the residual activity can be adjusted to a higher value through a continuous addition of makeup of fresh limestone, which in our case is not continuously added, since it was fed just to compensate for the material losses due to attrition and possible cyclone inefficient operation. The increase of the sorbent carrying capacity due to the addition of fresh limestone is shown in the figure 5 above.

4. Conclusion

Calcium looping experiments were performed in the 10kW$_{th}$ electrical heated IFK DFB facility using a natural limestone from South Germany. Realistic operating conditions were simulated for elevated partial

pressure of CO_2 up to 55vol. -% during regeneration. Realistic residence times up to 10 min as well as temperatures of 900 °C are shown to be sufficient for full sorbent regeneration. The sorbent CO_2 carrying capacity decays rapidly, but the observed residual activity of 8.5% is acceptable to maintain reasonable CO_2 capture efficiencies. Moreover, the experimental data follow the same trend as the ones used for validation of the model proposed by Charitos et al. [9] for the carbonator efficiency. The characteristic process parameter of active space time is proved to be the dominant one for process up-scaling purposes and it is found that a minimum value of τ= 50 s can be chosen for an efficiency of more than 85%.

Acknowledgements

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