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## Progress in Calcium Looping Post Combustion CO<sub>2</sub> Capture: Successful Pilot Scale Demonstration

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### Abstract

The development of Calcium-Looping for CO<sub>2</sub> capture has made vast progress in recent time. The technology has become a serious option for CO<sub>2</sub> capture from fossil fuel fired power plants. Calcium-Looping is a highly efficient process which uses broadly available natural limestone as a CO<sub>2</sub> sorbent. The process uses the reversible reaction ( $\text{CaCO}_3 \leftrightarrow \text{CaO} + \text{CO}_2$ ) between calcium carbonate and calcium oxide in the temperature range of 650 and 900°C. This publication presents the results of the work done at IFK to demonstrate the Calcium-Looping process in pilot scale at realistic process conditions. The first experimental campaigns with the 200 kW<sub>th</sub> Dual Fluidized Bed (DFB) Facility have shown hydrodynamic stability as well as high flexibility in operation. CO<sub>2</sub> capture efficiencies above 90 % were achieved consistently over a broad range of process conditions during multiple hours of operation. The presence of water vapor, which is found naturally in flue gas, was found to significantly improve the CO<sub>2</sub> capture efficiency. Sorbent attrition measurements fell within a reasonable range, giving confidence that attrition will not be a major restraint for Calcium Looping.

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Keywords: Calcium Looping; Carbonate Looping; Dual Fluidized Bed; CO<sub>2</sub> Capture; Pilot Plant; Wet Flue Gas; Water Vapor;

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### 1. Introduction

The Calcium Looping (CaL) process is rapidly becoming an important technologically feasible option for post-combustion CO<sub>2</sub> capture from fossil fuel fired power plants. This highly efficient technology is applied in Dual Fluidized Bed (DFB) systems and offers CO<sub>2</sub> capture efficiencies greater than 90 % with a comparatively low electric efficiency penalty of 6 % [9]. The CaL process utilizes natural limestone (CaCO<sub>3</sub>), which is widely available all over the world, as a sorbent for CO<sub>2</sub> capture. Under CaL process conditions, calcium carbonate calcination ( $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$ ) occurs at significant rates above 850°C.

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The reverse reaction allows CO<sub>2</sub> capture by CaO ( $\text{CaO} + \text{CO}_2 \rightarrow \text{CaCO}_3$ ) with the optimum temperature range lying between 600-650°C. The core process is operated as a continuous circuit of solids between two fluidized bed reactors: the carbonator for CO<sub>2</sub> capture, and the regenerator for sorbent calcination. As a post combustion CO<sub>2</sub> capture technology, the Calcium Looping Process can be retrofitted to existing fossil fuel fired power plants (Figure 1). Efficient capture of CO<sub>2</sub> can be achieved with a low oxygen demand in the regenerator compared to the carbon capture oxyfuel combustion process. In addition, heat can be recovered from the CaL process at high temperature levels for steam generation and electricity production (figure 1), increasing the overall electrical power output by 40-50 % based on the original power plant. Due to sorbent deactivation over time, a constant make-up stream of fresh limestone is necessary and (spent) purge material is removed. The purged sorbent (mainly CaO) can be utilized in the cement process and further reduce total CO<sub>2</sub> emissions.

After initial publication of the process idea by Shimizu et al. [13], the particle behavior over many calcination-carbonation cycles was investigated by thermo gravimetric analysis by several authors (e.g. [6], [11]), and subsequently the process was tested in electrically heated lab-scale facilities [4], [12]. Early key investigations in lab-scale facilities were carried out with different carbonator flow regimes in order to assess the effect of gas-solid contacting on the Calcium Looping process: (i) bubbling, (ii) turbulent, (iii) fast fluidized. Charitos [5] compared these three aforementioned regimes (using active space time vs. CO<sub>2</sub> capture efficiency as the criteria) and found that for the same active space time, turbulent and fast fluidized regimes had similarly excellent gas-solid contacting efficiencies with high CO<sub>2</sub> capture, whereas the bubbling regime had significantly less effective contacting and lower CO<sub>2</sub> capture. Technology development has now reached the pilot scale, requiring facilities which enable testing of the integrated plant as well as realistic process conditions (e.g. oxy-fired sorbent regeneration, effect of real flue gas, effects of fuel-ash and sulfur on sorbent performance and life-time, attrition, etc.). To this end, the first DFB Calcium Looping pilot plant designed for a 200 kW<sub>th</sub>-equivalent flue gas stream was built at the IFK, University of Stuttgart [10].

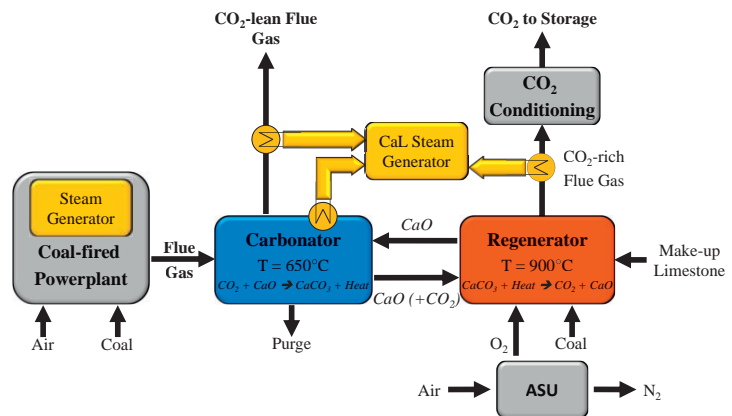


Fig. 1: Integrated Calcium Looping Process scheme.

## 2. Experimental Setup

A high degree of flexibility in the pilot plant configuration was set as a priority, allowing for a broad variation in process conditions for each configuration during the demonstration experiments thus enabling optimization of the plant design. To realize this, the 200 kW<sub>th</sub> Pilot Plant was designed for two different carbonator configurations, with a turbulent regime and a fast fluidized fluidization regime [8], [10].

### 2.1. Configuration of the 200 kW<sub>th</sub> Pilot Plant

Figure 2 shows the turbulent reactor configurations of the 200 kW<sub>th</sub> Calcium Looping pilot plant at IFK that was investigated within this work. This configuration offers potential advantages with respect to

operational flexibility and scale-up. The gas solid contacting behavior of the turbulent carbonator and its implications onto CO<sub>2</sub> capture is to be investigated.

The solid connection of the pilot plant, consisting of the turbulent fluidized bed carbonator (R2) and the fast fluidized circulating fluidized Bed (CFB) regenerator (R1), was achieved with the combination of an L-valve controlling the looping rate and a carbonator bottom loop seal. Based on the experimental and operational outcomes with regard to capture efficiency, process flexibility and hydrodynamic stability, recommendations for the further scale-up process can be given. The chosen design allows the control of solid looping rates independent of the CFB fluidization velocity which enables a broad variation of sorbent looping ratios (the molar fraction of circulating sorbent relative to the molar flow rate of CO<sub>2</sub> fed to the carbonator). The sorbent interconnection is achieved by an L-valve which is directly fed by the regenerator cyclone. Depending on the amount of L-valve fluidization, the solid transport between regenerator and carbonator can also be varied over a broad range of looping ratios. Excess solid flow from the regenerator overflows the L-valve stand pipe and circulates back internally into the regenerator. The transfer of sorbent from the carbonator to the regenerator is controlled by means of the bottom loop-seal.

The fast fluidized CFB regenerator (R1) has a height of 10 m and an inner diameter of 21 cm. The reactor is equipped with staged oxidant supply (O<sub>2</sub> and CO<sub>2</sub>) for optimized oxy-fired combustion with smooth temperature profiles over the whole reactor and correspondingly mild sorbent calcination conditions. The oxy-fired regenerator is designed for combustion with a global inlet concentration of up to 70 vol.-% O<sub>2</sub>, depending on the energy demand of the calcination reaction or the sorbent circulation rate between the carbonator and regenerator. In order to achieve realistic gas concentrations in the regenerator with respect to the flue gas humidity and CO<sub>2</sub> concentrations, flue gas recirculation is employed. The reactor has the capability for internal sorbent recirculation which increases the sorbent residence time and enables full sorbent calcination.

The carbonator (R2) is a 6 m turbulent fluidized bed with an inner diameter of 33 cm. The carbonator is designed for lower fluidization velocities than circulating fluidized bed reactors and less gas-solid contacting time compared to fast fluidized CFB operation although space times are similar. The removal of excess heat is achieved through a fluidized bed heat exchanger. Any sorbent entrained from the carbonator is recirculated via the upper loop seal and does not disturb process operation. Therefore, this configuration is expected to offer high operational flexibility with respect to power plant load variations (flue gas flow rate) with minor influence to the CO<sub>2</sub> capture efficiency at partial loads.

## 2.2. Analyses and metering equipment

In order to evaluate the experimental results adequately, it is essential to determine volume and mass flow rates. Therefore, all gas flows are controlled and continuously measured with mass flow controllers or flow meters. Gas concentrations are measured at different points of the facility. Besides the carbonator flue gas inlet concentration, both flue gas streams are analyzed by means of online gas analyzers. In order to investigate the CO<sub>2</sub> capture over the carbonator height, several probes are installed in the carbonator.

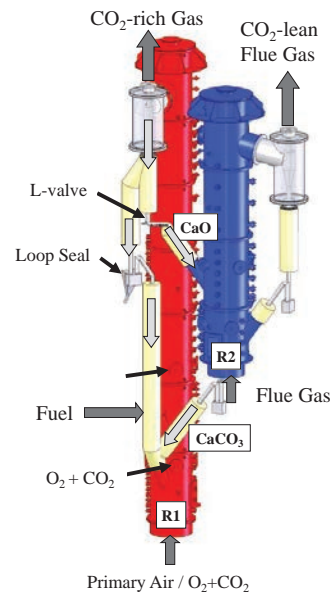


Fig. 2: Configuration of the 200 kW<sub>th</sub> DFB Pilot Plant.

The exact sorbent mass flow between the two beds is measured and converted into a sorbent looping ratio. Therefore, in each solid transfer pipe, mechanical measurement units are installed. Additionally an online measurement system for high temperature solid flow was developed at IFK which allows the monitoring of each circulation pipe and enables the precise control of sorbent flow between all reactors as well as internal recirculation leg.

The accurate and controlled supply of fuel to the combustor and regenerator as well as limestone make-up is important for the process to achieve constant experimental conditions. Loss-in-weight feeders are used for this purpose. The metering unit consists of a fuel feeder and a limestone feeder supplying the regenerator. Fuel and fresh limestone are directed through a rotary valve decoupling the reactor pressure level from the atmospheric metering system, and are fed close to the bottom of the regenerator.

Supplementary solid samples are taken from each reactor during and after steady state operating points to analyze the carbonated fraction of sorbent. Those measurements are carried out by means of thermo gravimetric analysis (TGA) after the experiments.

### 3. Experimental Experiences and Results

The 200 kW<sub>th</sub> pilot plant was designed to allow for a large variation in operating conditions, such as carbonator and regenerator temperatures, flue gas volume flows, sorbent looping ratios, carbonator space times (molar ratio of carbonator calcium inventory and incoming CO<sub>2</sub> in the flue gas) and make-up ratios (molar ratio of fresh CaCO<sub>3</sub> make-up and incoming CO<sub>2</sub> in the flue gas). Operational experiences as well as experimental results will be shown.

#### 3.1. Hydrodynamic behavior of the dual fluidized bed system

The main challenge within the pilot plant development process was to meet the required boundary conditions of the previously stated process parameters. These parameters mainly depend on the hydrodynamic behavior of the pilot facility.

Until now, experimental campaigns with over 600 hours of successful pilot plant operation have been completed. The facility is hydrodynamically stable as demonstrated over several days within one-week experimental campaigns.

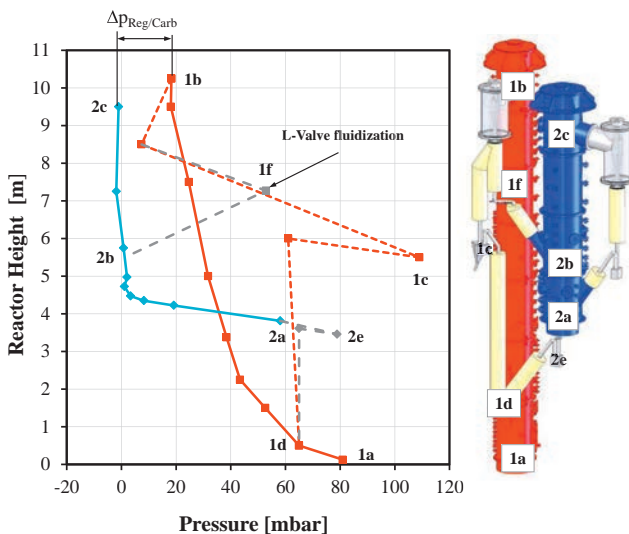


Fig. 3: Pressure profiles of both reactors and closed circulation paths.

of successful pilot plant operation have been completed. The facility is hydrodynamically stable as demonstrated over several days within one-week experimental campaigns. Carbonator and regenerator process parameters such as bed inventory and sorbent looping rates required for Calcium Looping were achieved. The temperature profiles were stable and uniform over time. The garnered long-term operational experience confirmed the robustness and self-stabilization of the system for similar operating points.

As described earlier, the dual fluidized bed system consists of a turbulent carbonator and a fast fluidized sorbent regenerator. In comparison, the carbonator is shorter, has a bigger diameter and with about 2 to 3 m/s is operated at lower fluidization velocities than the regenerator. This corresponds to a

turbulent fluidization pattern with minor entrainment but still good contact between gases and solids. The carbonator pressure profile (figure 3) shows a sharp increase in the lower region, which represents a carbonator inventory distribution shifted towards a dense region at the reactor bottom. The regenerator pressure profile shows a smoothly shaped curve in the bottom region and an almost linear gradient in the riser which represents a uniform distribution of inventory over the whole height enabling appropriate calcination conditions for the sorbent.

The target sorbent inventory distribution for a sufficient carbonator space time as the basis for efficient CO<sub>2</sub> capture was 2:1 between carbonator and regenerator. During the experimental investigations it was demonstrated that the inventory distribution could be adjusted through an increase in the overall reactor pressure towards the other reactor. For example an increase of the regenerator pressure results in increased carbonator bed inventory, since the bed mass must accumulate on the carbonator side to increase the standpipe pressure enough so as to overcome the increased pressure resistance at the bottom loop seal discharge side. The control of sorbent looping rate between the regenerator and the carbonator could be controlled by the degree of gas supplied to the L-valve. During long term experiments over several hours it was shown that stable operation of the system with constant sorbent looping ratios can be achieved given that the pressure between both reactor trains remains constant.

### 3.2. Temperature behavior

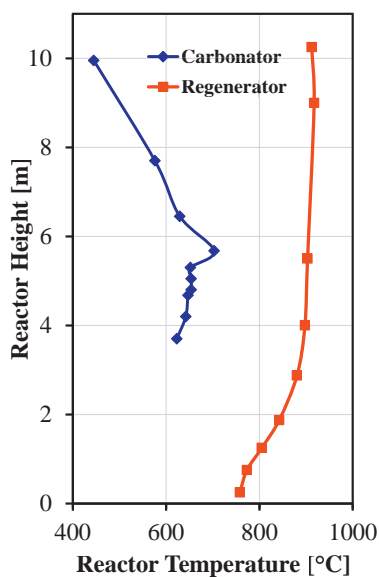


Fig. 4: Axial temperature profiles for carbonator and regenerator.

The heat supply of the endothermic calcination is realized through an internal oxy-fired combustion. The sorbent regenerator is designed to enable oxy-fuel combustion with flue gas recirculation as well as oxygen-enriched air combustion. In the first series of experiments, the focus was on the carbonation step in order to demonstrate the process and achieve high CO<sub>2</sub> capture efficiencies. Therefore, the sorbent regenerator was operated as oxygen-fired regenerator, combusting wood pellets with an oxygen-air mixture up to 50 vol.-% of oxygen.

The regenerator proved to be a very stable and efficient sorbent calciner allowing good temperature control. Figure 4 shows a typical temperature profile during coupled operation. It resembles the profile of a typical CFB combustor with a stable temperature level in the upper part and decreasing temperature in the bottom region, where colder material from the carbonator enters the reactor. The regenerator temperature typically ranged between 875-930°C. It can be seen that there are no local hot spots resulting from high oxygen concentration in the oxidant supply, due to secondary and tertiary oxidant-staging. The sorbent calcination in the regenerator showed high efficiency with full sorbent calcination as confirmed by thermo gravimetric analysis of the bed samples taken during experimental operation. The carbonator temperature profile is characteristic for the turbulent fluidization regime. While the dense bottom region of the reactor shows a temperature level of 650°C, the temperature decreases in the upper region due to the low sorbent entrainment. Nevertheless, this does not influence the CO<sub>2</sub> capture significantly, since the reaction takes place mainly in the dense region. A local temperature peak at approximately 1/3 of the total reactor height is caused by the incoming hot sorbent from the calciner which enters close to the temperature measurement and is as well not influencing the capture reaction.

### 3.3. Sorbent attrition

Limestone generally exhibits a high porosity, relatively low hardness thus attrites faster than other materials generally used in fluidized bed systems. The latest results from the 200 kW<sub>th</sub> Calcium Looping pilot plant at IFK have shown comparably low sorbent attrition rates during one week of operation. Dust filtered from both flue gas streams over the experimental period showed sorbent loss of less than 5 wt.-% of the total solid inventory per hour. The majority of fines were found in the regenerator flue gas indicating that the thermal stress of calcination and the mechanical stress in the cyclones are the main sources of attrition. Particle size measurements, carried out with laser diffraction particle sizing (Malvern Mastersizer) have shown a decrease of the mean particle diameter  $dp_{50}$  by 70  $\mu\text{m}$  from 370 to 300  $\mu\text{m}$  once steady-state conditions with respect to particle size are achieved. The sorbent sample was taken from the loop seal directly below the regenerator cyclone, which is considered to be the main source of attrition due to high velocities and the resulting mechanical stress in the vortex. The increased amount of fines below 100  $\mu\text{m}$  as observed by the particle size measurement verifies this assumption. The overall mass fraction of particles below the initial minimum diameter of 160  $\mu\text{m}$  was 10 %. These results indicate that sorbent attrition is relevant for future research work in pilot scale facilities since research surrounding sorbent behaviour in pilot facilities is currently still in its infancy. Future research aimed at enhanced sorbents either through sorbent pretreatment or the assessment of suitable sorbents, offers potential for reduced particle attrition. Improved process conditions, especially in the regenerator will help to minimize particle decay and attrition. That said, the amount of material lost due to attrition is still less than the amount of limestone make-up required to maintain an active bed material for high CO<sub>2</sub> capture and does not negatively influence the process.

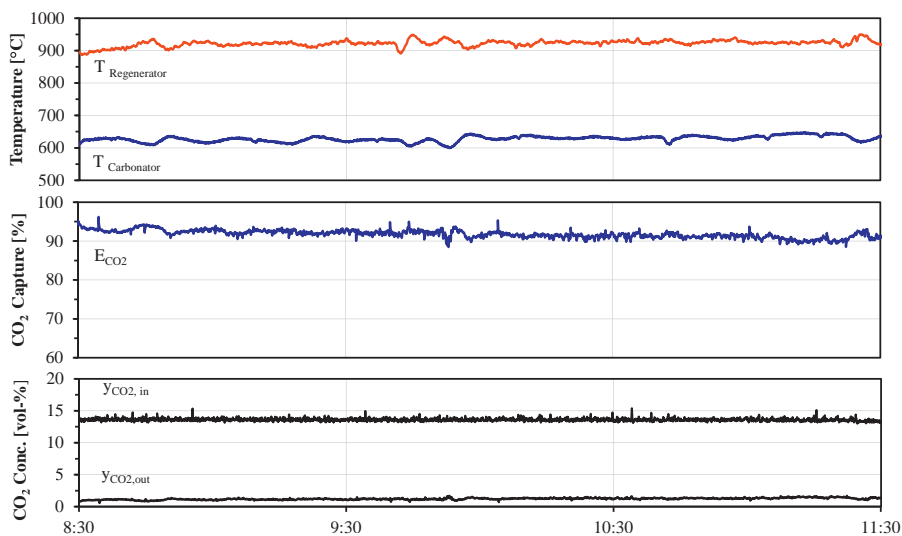


Fig. 5: Operating period with CO<sub>2</sub> capture efficiency above 90 %. The inlet flue gas contains typical water vapor concentrations of 14 %.  $E_{\text{CO}_2}$ = Capture Efficiency;  $y_{\text{CO}_2\text{in}}$ = inlet CO<sub>2</sub> concentration (wet);  $y_{\text{CO}_2\text{out}}$ = outlet CO<sub>2</sub> concentration (wet).

### 3.4. Process demonstration with high CO<sub>2</sub> capture efficiency

The main achievement of recent Calcium Looping research at IFK has been the process demonstration at the pilot plant scale with CO<sub>2</sub> capture efficiencies over 90 % for a broad range of operating conditions.

Furthermore, an evaluation of optimal process operating points through variation of carbonator temperature and sorbent looping ratios was carried out. The experiments were carried out with a CO<sub>2</sub> inlet concentration of around 14 vol.-% in a synthetic flue gas. In the first series of experiments dry flue gas was used. To simulate a more realistic flue gas with approximately 14 vol.-% of water vapor, which is common for flue gases after flue gas desulfurization, steam was added to the flue gas.

Figure 5 shows an operating period of 3 h at carbonator temperatures between 600-650 °C. The average CO<sub>2</sub> outlet concentration over the whole duration could be kept below 2 % which corresponds to a CO<sub>2</sub> capture efficiency of more than 90 %. Small changes in carbonator temperature and looping ratio were made in order to investigate the effect of chemical equilibrium and reaction rate on the CO<sub>2</sub> capture efficiency. In this was found that minor temperature fluctuations of 10 °C in the range of 620 to 650 °C do not have a significant negative effect onto the CO<sub>2</sub> capture efficiency. However, temperatures below and above do influence CO<sub>2</sub> capture. Hence actions to minimize temperature fluctuations have to be undertaken.

### 3.5. Effect of flue gas humidity

Additional experiments were carried out to investigate the influence of temperature on capture efficiency in the range of 590 to 680 °C. Each experimental point represents a single steady state where process conditions were kept constant for at least 30 minutes. For these points, solid samples were taken, analysed and looping rates were measured. Changing between two steady state temperature levels was achieved by varying the looping rate, usually within 15 minutes. Therefore, lower looping ratios correspond to lower temperatures, while higher temperatures require increasing looping ratios.

The steady-state capture efficiency values for dry and wet flue gas are shown in figure 6 along with the equilibrium capture efficiency curve for a CO<sub>2</sub> inlet concentration of 14 vol.-%. As predicted by theory, the equilibrium CO<sub>2</sub> capture efficiency drops with increasing temperature, thus limiting the maximum possible capture efficiency. Previous results from lab scale facilities [4] testing with dry flue gas have shown a decrease of capture efficiency for temperatures below 630 °C. These results have been replicated on the pilot facility. However, the opposite trend was seen for wet flue gas with 14 % vol.-% of water vapor, which is a representative concentration after flue gas desulfurization. It was found that the CO<sub>2</sub> capture efficiency increases with decreasing temperature, following the trend of the equilibrium curve until 600 °C, even though looping ratios were decreasing as well. These results prove the findings of TGA analyses carried out from different authors [2], [3], [11]. The authors showed that water vapor catalyses the carbonation and increased CaCO<sub>3</sub> conversion of the sorbent can be achieved. Due to the authors different mechanisms are conceivable: The formation of a transient compound Ca(OH)<sub>2</sub> as an

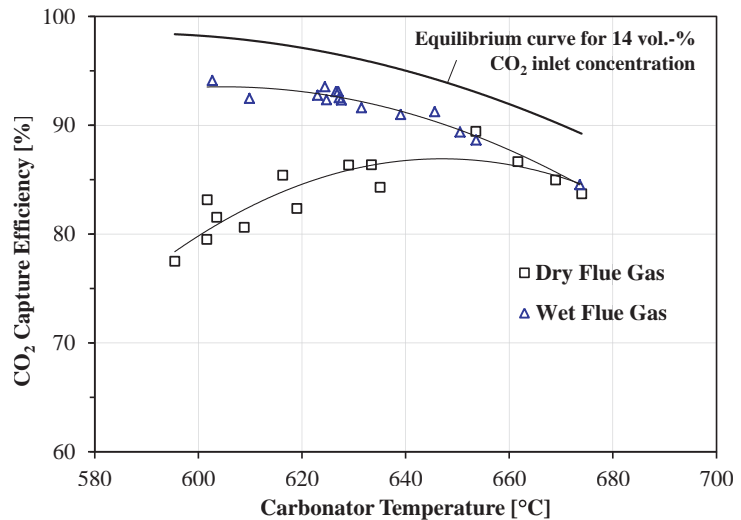


Fig. 6: Temperature influence for dry and wet flue gas conditions.

intermediate reaction step (i), enhanced conversion due to reduced diffusion resistance with water vapour (ii) and the formation of increased pore sizes due to water vapor enhanced sintering during calcination (iii). TGA experiments at IFK have also shown increased  $\text{CaCO}_3$  conversion due to water vapor, mainly in the diffusional reaction regime. It could be perceived that the difference in  $\text{CO}_2$  capture capacity between dry and wet flue gas increases with the number of calcination-carbonation cycles, although the overall capture capacity decreases with the number of cycles. In a continuous process this effect can compensate the decay of sorbent capacity especially for low fresh limestone make-up rates and low circulation rates since reaction takes place predominantly in the diffusional reaction regime.

Within the experiments with the 200 kW<sub>th</sub> pilot plant this effect could be shown clearly. It could be observed that the capture efficiency increases significantly and without delay after changing the flue gas humidity from 0 % to 14 % in the carbonator. It also indicates that mechanisms (i) or (ii) are most likely since water vapor enhanced sintering is considered to be a slow process, however this does not exclude that pore size growth through vapor enhanced sintering takes place and increases the average sorbent capacity.

As a consequence, the effect of wet flue gas, as proved in pilot operation, offers extended potential for process operation, and also for energy savings since high  $\text{CO}_2$  capture rate can be reached with lower looping ratios (thereby requiring less fuel for the regenerator). The measured capture efficiencies lie relatively close to the equilibrium curve indicating good gas-solid contact in the turbulent fluidized bed carbonator, but showing potential for further optimization (e.g. with CFB carbonators).

#### 4. Conclusion

At IFK, University of Stuttgart, a 200 kW<sub>th</sub> dual fluidized bed facility for calcium looping was developed. The 200 kW<sub>th</sub> pilot plant is hydrodynamically stable and allows for a broad range of operating conditions. During the first experimental campaigns, the Calcium Looping process was demonstrated under pilot plant conditions for the first time. The process and pilot plant operation proved to be robust, stable, and easy to control. Full calcination of carbonated sorbent and fresh limestone was achieved in the oxygen-fired regenerator with inlet oxygen concentrations up to 50 vol-%. The rate of total solid inventory loss due to sorbent attrition was measured to be less than 5 wt.-% per hour which is less than the make-up limestone expected to maintain a constant bed activity.  $\text{CO}_2$  capture efficiencies above 90 % were achieved over a wide range of temperatures and calcium looping ratios. The addition of water vapor, which is naturally present in flue gas, significantly improved the  $\text{CO}_2$  capture efficiency.

#### Acknowledgements

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