CALCIUM LOOPING FOR CO₂ CAPTURE IN THE CEMENT INDUSTRY – PILOT SCALE EXPERIMENTS
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Abstract – Calcium looping has been demonstrated to be a promising technology for CO₂ capture in fossil fuel fired power plants for reasons such as its high energy efficiency. Since both processes use a calcium rich material that is calcined, there are immanent synergies between the calcium looping process and cement production. Therefore, the calcium looping process is highly suitable as a CO₂ capture process for the cement industry. In this work, experimental results from tests using calcium looping operational conditions that match the requirements of the cement plant in an ideal way are presented. In this context, the process was operated with high make-up rates that generate also a high process purge for utilization in the cement process. With such a configuration, CO₂ capture rates above 95% could be accomplished.

INTRODUCTION
It is widely agreed that anthropogenic greenhouse gas emissions e.g. CO₂ accelerate the climate change. The cement industry is one of the largest industrial CO₂ emission sources, responsible for approximately 5% of the world’s anthropogenic CO₂ emissions (IEA, 2009). Approximately 60% of the CO₂ emissions are inherent to cement production, since they arise from calcination of CaCO₃ to CaO a precursor of clinker. Hence, CCS technologies (post combustion and oxy-fuel) are considered to decarbonize the cement industry (IEA 2009).

Calcium looping was originally proposed by Shimizu et al. (1999) and has emerged rapidly in the recent years. By today the calcium looping technology has been demonstrated up to pilot scales with flue gas streams equivalent to firing capacities of 200 kW to 1.7 MW (Alonso et al., 2014; Arias et al., 2013; Dieter et al. 2014; Ströhle et al., 2014). The calcium looping process is a solid sorbent based, high temperature, post combustion CO₂ capture process using limestone (CaCO₃) or other Ca-based materials as sorbents. Generally, the calcium looping process is operated in a dual fluidized bed system, even though under certain conditions, also entrained flow systems may be an interesting option. The reaction on which the calcium looping process is based is the calcination-carbonation equilibrium between CaO and CaCO₃ (eq. 1). This reaction requires an input of heat (178.2 kJ/mol_CaCO₃) for the calcination that is released during carbonation.

\[
\text{CaCO}_3 \leftrightarrow \text{CaO} + \text{CO}_2 \quad \Delta R H = +178.2 \frac{kJ}{mol}
\]  

By means of cyclic carbonation and calcination (or regeneration) of the sorbent, CO₂ can be captured in solid carbonate form and hence be easily separated from the flue gas with a cyclone. This capture takes place in the carbonator, which is operated around 650 °C. In this reactor, the regenerates sorbent (CaO) reacts with CO₂ from the flue gas in an exothermic reaction and forms CaCO₃. This CaCO₃ (i.e. the loaded sorbent) is separated from the flue gas that is depleted of CO₂ and sent to the regenerator. In the regenerator, heat is provided by means of fuel combustion to decompose CaCO₃ to CaO and CO₂. The regenerator is operated in oxy-fuel combustion mode to generate a highly concentrated CO₂ stream. Under these CO₂ rich conditions, temperatures slightly above 900 °C are required for sorbent regeneration/calcination. Due to the high temperature level of this CO₂ capture process the heat required for sorbent regeneration can be recuperated efficiently by the means of a highly efficient steam cycle. Due to the efficient heat recovery, the energy penalty of the calcium looping CO₂ capture process for power plant application is low compared to other CO₂ capture processes (Abanades et al. 2005). With an increasing number of calcination and carbonation cycles the sorbent’s CO₂ carrying capacity decreases. Therefore, used sorbent has to be continuously replaced by fresh sorbent to obtain a constant CO₂ capture performance.

The CO₂ capture efficiency of the calcium looping carbonator is defined as follows:

\[
E_{CO₂} = \frac{\dot{N}_{CO₂,Carb,in} - \dot{N}_{CO₂,Carb,out}}{\dot{N}_{CO₂,Carb,in}}
\]

(2)

where \(\dot{N}_{CO₂,Carb,in}\) is the molar flow of CO₂ entering and \(\dot{N}_{CO₂,Carb,out}\) is the molar flow of CO₂ leaving the carbonator. In practical systems, CO₂ capture is limited by the available reaction time, the incoming amount of sorbent (i.e. reactive CaO) or by the reaction temperature or more accurately by the equilibrium CO₂ partial
pressure of the calcination-carbonation equilibrium at this temperature. In that way, the calcination-carbonation equilibrium defines the minimum achievable CO₂ partial pressure within the carbonator (and at its outlet) as a function of temperature, and consequently the maximum achievable CO₂ capture.

Assuming sufficient residence time of the particle to react in the carbonator, the CO₂ capture performance of the calcium looping process can be described by the following two key parameters. The looping ratio, which is defined as the molar ratio between CaO and CO₂ entering the carbonator (N_{CaO}/N_{CO₂}) and the make-up ratio, which is defined as the molar ratio of fresh CaO entering the system with the sorbent make-up stream (N_{CaO,m}/N_{CO₂}). To obtain a higher CO₂ capture efficiency, a higher availability of active sorbent needs to be present in the carbonator. This can be achieved by circulating more material between the reactors (i.e. increase of looping ratio) or by increasing the CO₂ capture activity of the circulating bed material (increase of make-up ratio).

In calcium looping applications for CO₂ capture from power plants a minimization of the make-up rate is desirable to reduce costs of fresh sorbent and solid residue handling and disposal. However, in case of CO₂ capture from a cement plant, the incoming amount of fresh sorbent can be significantly increased, since the spent sorbent purified from the process can be further utilized as raw material for the clinker production. In this context, high make-up rates induce a highly active bed material. Depending on the sorbent activity, a certain amount of CaO must be circulated between the carbonator and regenerator to provide active sorbent for the CO₂ capture in the carbonator. Hence, the circulating flow (i.e. looping ratio) between the regenerator and carbonator can be reduced with increasing make-up ratio.

Since both processes use raw materials containing mainly CaCO₃, synergies between the cement production and CaL process seem evident and have been identified by various research groups (Dean et al., 2011; Perejón et al., 2016). However, most of these synergies have only been assessed theoretically. In this work these synergies are experimentally investigated.

**EXPERIMENTAL SETUP**

The results presented in this work have been obtained at the 200 kWₘ fluidized bed calcium looping pilot facility of the Institute of Combustion and Power Plant Technology (IFK) at University of Stuttgart. The pilot plant consist of three refractory lined reactors two of which allow operation in circulating fluidized bed (CFB) mode and one can be operated as a turbulent fluidized bed (TFB). These reactors can be interconnected to test the calcium looping process in a CFB-CFB, but also in a TFB-CFB reactor configuration. While the regenerator is always operated in CFB mode, the carbonator can be operated either in TFB mode or in CFB mode (see figure 1). Both CFB reactors are 10 m in height and have an inner diameter of approximately 20 cm. The TFB reactor is 6 m in height with an inner diameter of 33 cm. Temperatures and pressures are measured along the height of the reactors, return legs and exhaust lines. Each reactor’s exhaust gas line consists of a protective (secondary) cyclone and a bag filter. In case of calcium looping operation, fuel and limestone are continuously fed into the regenerator by the means of a rotary valve. The dosing of the solids is gravimetrically controlled. Spent sorbent is purged by the means of an extraction system. For oxy-fuel operation of the regenerator, CO₂ rich regenerator off gas is recycled and mixed with oxygen for combustion of coal in this reactor. The carbonator is fed with a synthetically mixed flue gas generated by mixing CO₂, steam and air.

In CFB-CFB configuration, the circulation rate is controlled by the means of two cone valves and the material circulation is measured by microwave sensors, which are manually calibrated. Indifferent to that, in TFB-CFB configuration, the circulation rate is adjusted by a conveyer screw and the fluidization of the carbonator’s bottom loop seal. To evaluate the calcium looping process performance in these experiments, the gas composition (CO₂, O₂, SOₓ, NOₓ, H₂O) is measured at the carbonator and regenerator outlet as well as at the carbonator inlet. Furthermore, solid samples are taken from the loop seals, the protective cyclones and the bag filter.

Two experimental campaigns were conducted using the two different reactor configurations to assess the calcium looping operation under cement specific operational conditions, i.e. high make-up rates. Make-up ratios between 0.5 and 1.4 mol_{CaO}/mol_{CO₂} have been investigated. The regenerator was oxy-fuel fired using two different Colombian coals differing mainly in sulfur content. As sorbent, a limestone from western Germany with a nominal particle size between 100 – 300 µm was used. The solids’ compositions are shown in table 1 and table 2. In the carbonator, a humid flue gas with a CO₂ concentration of 15 % was investigated. This is justified by the assumption that the cement plant’s raw meal is fully decarbonized within the calcium looping process before entering the kiln.
Table 1: Composition of the two coals used in the calcium looping tests (Colombian I: TFB-TFB; Colombian II: TFB-CFB).

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<tbody>
<tr>
<td>Colombian I</td>
<td>73</td>
<td>4.4</td>
<td>1.7</td>
<td>0.6</td>
<td>11</td>
<td>9.6</td>
</tr>
<tr>
<td>Colombian II</td>
<td>71</td>
<td>4.8</td>
<td>1.4</td>
<td>1.0</td>
<td>13</td>
<td>9.1</td>
</tr>
</tbody>
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Table 2: Composition of the limestone used in both calcium looping test campaigns.

<table>
<thead>
<tr>
<th>Limestone</th>
<th>CaCO₃ [wt%, ar]</th>
<th>MgCO₃ [wt%, ar]</th>
<th>SiO₂ [wt%, ar]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Western Germany</td>
<td>92</td>
<td>1.9</td>
<td>5.7</td>
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Fig. 1: IFK’s 200 kWₜ fluidized bed pilot facility in a) CFB-CFB configuration and b) TFB-CFB configuration.
RESULTS AND DISCUSSION

CO₂ capture efficiency:

In Figure 1, the CO₂ capture efficiency obtained during experiments both (TFB-CFB and CFB-CFB) experimental campaigns are plotted against the carbonation temperature, together with the (maximum) equilibrium CO₂ capture at 15 vol% CO₂ flue gas concentration. Each test point was stably operated for at least one hour. It can be seen that for most tests the CO₂ capture is limited by the carbonation temperature i.e. the equilibrium CO₂ partial pressure, since the maximum possible CO₂ capture efficiency could practically be reached. This indicates that a sufficient amount of active sorbent was present in the carbonator. For all investigated make-up ratios, it was found that a looping ratio of 10 molCaO/molCO₂ is sufficient to achieve CO₂ capture rates near the equilibrium CO₂ capture rates. The calcination degree of the sorbent leaving the regenerator averaged at approx. 96 % in the CFB-CFB campaign, whereas the calcination degree averaged at approx. 98 % for the TFB-CFB campaign. These results are consistent with the respective carbonation degrees of the sorbent leaving the carbonator. The carbonation degree averaged at approx. 12.8 % for the CFB-CFB campaign and approx. 11.1 % for TFB-CFB campaign.

![Fig. 2. Carbonator CO₂ capture efficiency vs. carbonator temperature for CFB-CFB configuration (marked with circles) and TFB-CFB configuration (marked with squares). In addition, the CO₂ equilibrium capture efficiency (dashed line) is plotted.](image)

Characteristic particle size distribution:

Figure 3 shows the particle size distributions of the regenerator and carbonator loop seals, as well as the respective protective cyclones, bag filters and the used raw limestone for the TFB-CFB and CFB-CFB operation. With respect to the raw limestone, the particle size in the bed decreased due to fragmentation and attrition. It can also be noted that fine particles are exiting the calcium looping process via protective cyclones and bag filters. For both reactor configurations (CFB-CFB, TFB-CFB), the bed material’s average particle size (d₅₀) in the carbonator and regenerator were approximately 165 μm. Particles below 10 μm were poorly separated by the cyclones and therefore lost from the fluidized bed system and retained by the bag filters. Since the fluidization velocity is reduced in the TFB-CFB configuration, only finer particles are entrained in this setup and the particle size distribution of the material extracted from the TFB carbonator’s protective cyclone is shifted to lower particle sizes.
Fig. 3. Average particle size distribution of all solid samples (i.e.: loop seals, 2nd cyclones and bag filters of the respective reactor) taken during the experimental campaigns: a) conducted in CFB-CFB mode and b) conducted in BFB-CFB mode, with raw limestone as reference.

Regenerator operation with high make-up rates:

Higher make-up rates of limestone and hence a higher purge streams of solids from the system require an increased heat demand in the regenerator since the additional material needs to be calcined in the endothermic calcination reaction which represents an energy sink. This issue has been addressed by increasing the fuel feed to the regenerator compared to a standard calcium looping configuration with lower make-up ratios. To maintain a constant gas velocity in the regenerator, the oxygen content in the oxidizer (oxygen mixed with hot recycled CO$_2$ rich regenerator off gas) had to be increased accordingly. Oxygen inlet concentrations of approx. 55 vol% were required to ensure a regenerator temperature of 920 °C at a velocity of 4 m/s. The calcination reaction moderates the temperature profile in the regenerator resulting in uniform temperature profiles along its vertical axis. An exemplarily temperature profile of the regenerator is shown in figure 4a. The temperature was approx. 860 °C at the bottom of the regenerator were colder solids from the carbonator are entering (at 0.5 m). The corresponding trend of the measured gas concentrations over time on dry basis and the regenerator temperature is shown in figure 4b-d. The hourly peaks of the gas measurements correspond to cleaning of the sample gas filters.

Fig. 4. Regenerator operation with high oxygen inlet concentration: a) Temperature profiles of the carbonator and regenerator, and trend of b) regenerator temperature, c) O$_2$ inlet and CO$_2$ outlet concentrations of the regenerator and d) O$_2$ outlet concentration of the regenerator.
CONCLUSION

Cement specific calcium looping operational conditions (i.e. high make-up rates) have been investigated during two experimental campaigns at IFK’s 200 kWth fluidized bed pilot facility using a CFB-CFB and a TFB-CFB reactor configuration. Both reactor designs CO₂ capture rates of up to 98 % have been achieved, indicating that the CO₂ capture was limited only by the carbonation temperature or the equilibrium capture, respectively. The supplementary energy demand of the calcination of additional make-up in these tests was compensated by increasing the oxygen inlet concentration into the regenerator. The experimental findings substantiate that the calcium looping process is very suitable for CO₂ capture from cement plants.

NOTATION

ΔH  reaction enthalpy, kJ/mol
Nᵢ  molar flow of component i, kmol/h
E_{CO2}  CO₂ capture efficiency, %
d_{p50}  mass median diameter, µm

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