1 MW TH LONG-TERM PILOT TESTING OF THE CARBONATE LOOPING PROCESS WITH HARD COAL AND LIGNITE

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Abstract – The calcium carbonate looping (CaL) process is an efficient post-combustion carbon capture technology to reduce the emitted amount of carbon dioxide (CO2) by fossil fueled power and industrial plants. The presented work discusses the results gained in four test campaigns, each four weeks long, performed in a 1 MWth CaL pilot plant at Technische Universität Darmstadt with coal originated flue gas from a coal fired furnace. The calciner was fired in oxy-fuel combustion mode, i.e. coal was burned with oxygen and flue gas was recirculated to moderate the temperature. The objective of these test campaigns was to improve the process and to gain reliable experimental data to scale up the CaL process to industrial size. The type of fuel, sorbent, flue gas composition, reactor design, and operating conditions were varied to investigate long-term effects on the performance during pilot operation. Steady-state conditions were achieved while parameters were not changed during periods up to 60 hours. The feasibility of the CaL process in industrial size was proven by steady-state CO2 absorption for more than 1,219 hours with interconnected circulating fluidized bed reactors and capture rates up to 94 %. Keywords – calcium looping, CO2 capture, pilot plant, dual fluidized bed, oxy-fuel regenerator

INTRODUCTION

An increase of the energy demand for the next decades is expected and fossil fuels as coal and natural gas will remain a major energy source for power production to cover the need (OECD/IEA, 2015a). The availability in large quantities in many areas worldwide ensures the power supply. Nevertheless, the knowledge about climate changes increased during the previous decades and it has been proven that global warming is mainly caused by the anthropogenic release of greenhouse gases. The effect of the greenhouse gas CO2, inevitably formed and released in significant amounts by combusting fossil fuels, and its contribution to the global warming is generally accepted (OECD/IEA, 2015b). Capture and Storage (CCS) has been identified as an important contribution for mitigation of CO2 emission of fossil fueled power plants (European Commission, 2015; OECD/IEA, 2015a). Various CO2 capture processes to reduce the amount of CO2 emitted by fossil fueled power and industrial plants have been proposed, developed and investigated. First generation CO2 capture technologies, e.g. Mono-Ethylene-Amine Scrubbing (MEA, post-combustion), Integrated Gasification Combined Cycle (IGCC, pre-combustion) or Oxy-Fuel Combustion have the disadvantage of crucial net efficiency losses in a range of 9-14 %-points (Abu Zahra et al., 2011; Martelli et al., 2009). Hence, various second generation CO2 capture processes are currently being developed aiming at improved efficiencies. The CaL process is characterized by a low net efficiency penalty of 5-7 %-points including CO2 compression, low CO2 capture costs below 30 €/tCO2 and low environmental impact (Eyple and Ströhle, 2008). The CaL process has also aroused the interest of the cement industry during the last decade since spent sorbent based on the limestone used in the CO2 capture process could be utilized as raw material for clinker production.

The CaL process is a post-combustion CO2 capture technology using limestone based sorbents and was initially proposed by Shimizu et al. (1999). The CO2 contained in the flue gas from an emission source is absorbed by calcium oxide (CaO) in the carbonator in an exothermic reaction at around 650 °C and transferred as calcium carbonate (CaCO3) to the calciner. By increasing the temperature up to around 900 °C, the CO2 bound in the solid phase, is released in an endothermic reaction. The heat for the endothermic calcination reaction can be provided in the directly heated Cal process by oxy-fuel combustion of fuel (e.g. coal) or in the indirectly heated Cal process (IHCaL) via heat transfer (e.g. heat pipes) from another reactor (Reitz et al., 2016). A gas stream of highly concentrated CO2 leaves the calciner, while the CaO is returned to the carbonator. The reaction can be described by Eq. (1):

\[
\text{CaO}_{(s)} + \text{CO}_2{_{(g)}} \rightleftharpoons \text{CaCO}_3{_{(s)}} \quad \Delta H_{298^\circ C} = \pm 178.2 \text{ kJ/mol} \quad (1)
\]

Since the basis concept was proposed, various research groups worldwide spent effort in the investigation of the CaL process and various pilot plants with increasing capacity were built. At the University of Stuttgart, a
200 kW\textsubscript{e} pilot plant was raised. The Institute for Energy Systems and Technology (EST) at Technische Universität Darmstadt erected a 1 MW\textsubscript{th} CaL pilot plant. The first continuous 1 MW\textsubscript{th} CaL pilot scale operation in an interconnected circulating fluidized bed (CFB) system was achieved. Additional test campaigns were conducted using natural gas or coal in the calciner (Ströhle et al., 2014). Also a 1.7 MW\textsubscript{th} CaL pilot plant was built in La Pereda (Spain) decarbonizing flue gas from a nearby power plant achieving high capture rates (Arias et al., 2013).

The present paper summarizes the main experimental results from four long-term CaL test campaigns carried out in the 1 MW\textsubscript{th} pilot plant at Technische Universität Darmstadt with the aim to optimize operability as well as to gain a reliable data base for process scale-up to industrial size. The experimental tests were particularly focused on the long-term sorbent reactivity in realistic operating conditions such as oxy-fuel combustion in the calciner to guarantee a high CO\textsubscript{2} concentration in order to gain reliable information about the sorbent deactivation during various capture cycles of the limestone at realistic calcination conditions. During the test campaigns, the type of fuel (hard coal, lignite in various particle size distributions), the sorbent, flue gas composition, reactor design and operating conditions, e.g. reactor temperatures, make-up flow, solids circulation flow etc., were varied to investigate long-term effects on the performance (Helbig et al., 2016). Steady-state operation decarbonizing the flue gas of a 1 MW\textsubscript{th} coal fired furnace was investigated during 2,400 hours of operation, thereof 1,219 hours with continuous CaL operation capturing CO\textsubscript{2}.

**EXPERIMENTAL**

A semi-industrial scale CaL pilot plant consisting of two interconnected circulating fluidized bed reactors and a combustion chamber with a thermal capacity of 1 MW\textsubscript{th} each is located at Technische Universität Darmstadt. The scheme of upgraded 1 MW\textsubscript{th} CaL pilot plant at Technische Universität Darmstadt is shown in Fig. 1. The carbonator has an inner diameter of 600 mm and is 8.6 m high. The dimensions of the calciner are 400 mm and 11 m, respectively. The plant design is illustrated in Fig. 1. The plant is equipped with all conventional components of typical industrial CFB systems. The combustion chamber provides the coal originated flue gas for the carbonator. The mass flow between the coupled fluidized bed reactors is controlled by a screw conveyor. In order to reach realistic oxy-fuel conditions, the calciner is fired with oxygen enriched recirculated flue gas. The heat release of the carbonation reaction can be extracted directly from the carbonator bed by means of five axially arranged internal cooling tubes. The flue gases are cooled down by means of two-pass heat exchangers. The entrained solid particles are removed from flue gases in bag filters.

![Scheme of upgraded 1 MW\textsubscript{th} CaL pilot plant at Technische Universität Darmstadt.](image)

Fig. 1. Scheme of upgraded 1 MW\textsubscript{th} CaL pilot plant at Technische Universität Darmstadt.
The inventory of solids in the carbonator and calciner is continuously determined by the measurement of the reactor pressure drop between the plane above the distributor and the exit of the reactor. The average composition of the solids entering and leaving the calciner is defined by the chemical equilibrium. The chemical equilibrium is a function of the solid composition determined by solid analysis. Gas compositions and volumetric flows of the inlet and outlet gas streams are measured. The solid mass flow circulating between the calciner and the carbonator leaving is frequently determined from solid sampling.

The relationship between the captured CO₂ fraction given by the chemical equilibrium and the average carbonator temperature is shown in Eq. (3) from Silcox et al. (1989):

\[ \nu_{\text{CO}_2,\text{in}} = 4.137 \times 10^7 \exp \left( \frac{-20,474}{T} \right) \]  

The total CO₂ capture efficiency for the CaL process is defined as the relationship between the captured CO₂ at the calciner outlet (F_{CO₂,calc,out}) and produced CO₂. The total amount of produced CO₂ includes the CO₂ fed from the host plant (F_{CO₂,coal}) as well as CO₂ formed by combustion of coal in the calciner (F_{CO₂,calc}), shown in Eq. (4).

\[ E_{\text{total}} = \frac{F_{\text{CO}_2,\text{calc,out}}}{F_{\text{CO}_2,\text{in}} + F_{\text{CO}_2,\text{0}} + F_{\text{CO}_2,\text{coal}}} \]  

Four comprehensive long-term CaL test campaigns of four weeks each were conducted. Test campaigns #1 and #3 were performed with hard coal either in pulverized (d₅₀ ~ 36-45 μm), coarser pulverized (d₅₀ ~ 500 μm) and coarse form (d₅₀ ~ 1500 μm), test campaigns #2 and #4 with pulverized (d₅₀ ~ 35 μm) or grained lignite (d₅₀ ~ 500 μm) respectively. During these test campaigns, two different sorbents from western (LimestoneA, d₅₀ ~ 180 μm) and southern (LimestoneB, d₅₀ ~ 215 μm) Germany with different chemical compositions and particle size distributions were utilized. Table 1 presents an overview of the test campaigns including the number of test campaigns, performed between September 2015 and April 2016, the operating conditions, and the fuel of the calciner and the sorbent used for the tests.

<table>
<thead>
<tr>
<th>Calciner fuel</th>
<th>Calciner fuel size</th>
<th>Calciner mode</th>
<th>Sorbent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 hard coal</td>
<td>coarse</td>
<td>d₅₀ ~ 1500 μm</td>
<td>oxy-fuel fired</td>
</tr>
<tr>
<td>1 hard coal</td>
<td>pulverized</td>
<td>d₅₀ ~ 45 μm</td>
<td>air / oxy-fuel fired</td>
</tr>
<tr>
<td>2 lignite</td>
<td>pulverized</td>
<td>d₅₀ ~ 35 μm</td>
<td>oxy-fuel fired</td>
</tr>
<tr>
<td>3 hard coal</td>
<td>pulverized</td>
<td>d₅₀ ~ 36 μm</td>
<td>oxy-fuel fired</td>
</tr>
<tr>
<td>4 lignite</td>
<td>pulverized</td>
<td>d₅₀ ~ 35 μm</td>
<td>oxy-fuel fired</td>
</tr>
<tr>
<td>4 lignite</td>
<td>grained</td>
<td>d₅₀ ~ 500 μm</td>
<td>oxy-fuel fired</td>
</tr>
</tbody>
</table>
The detailed evaluation including heat and mass balances as well as detailed sorbent analysis aims to gain a deeper understanding of the CaL process with a distinguished focus to apply the experimental data for scaling-up the CaL process to a realistic demonstration plant.

RESULTS AND DISCUSSION

Steady-state and transition periods from long-term pilot testing are exemplarily shown in Fig. 2. Generally, an experimental test campaign starts with heating of the reactors by start-up burners and coal, calcination of the solid inventory and start of flue gas recirculation in the calciner. Then operating conditions, e.g. make-up flow, coal feed, solid circulation etc. are adapted to adjust the operating conditions. Sorbent activity needs to be adjusted as well as loss of fines due to attrition has to be replaced by make-up addition.

Exemplary results from a CaL long-term test campaign in the 1 MWth pilot plant of TU Darmstadt are shown in Fig. 2 a-c. In the initial period until hour 35 (1), the CaL process was started. Temperatures $T_{\text{calc}}$ of 900°C in the calciner and $T_{\text{carb}}$ of 650 °C in the carbonator were adjusted (Fig. 2b). The reactor velocities $u_{\text{calc}}$ and $u_{\text{carb}}$ were kept around 5 m/s in the calciner and 3 m/s in the carbonator, respectively (Fig. 2b). The specific carbonator inventory $W_{\text{S,carb}}$ was 500 kg/m$^2$ (Fig. 2c). The solid circulation rate between the reactors $G_S$ was increased to 3.9 kg/m$^2$s (Fig. 2c) and the make-up flow rate $F_0$ was increased from 0.18 to 0.38 mol/m$^2$s (Fig. 2a) with the aim to achieve a carbonator absorption rate $E_{\text{carb}}$ higher 80 % (Fig. 2a).

In the period from hour 35 (1) to hour 53 (2), CO$_2$ was continuously captured in the set range of parameters. The flow of CO$_2$ captured in the carbonator $F_{\text{CO2,carb,in}} \times E_{\text{carb}}$ increased up to 4.1 mol/m$^2$s leading consecutively to $E_{\text{carb}}$ higher 80% (Fig. 2a).

![Fig. 2. Exemplary period of long-term CaL tests.](image-url)
The continuous operation was interrupted at hour 53 (2). Blockings in the carbonator cyclone led to a discontinuous internal solid circulation in the system and inventory was discharged via cyclone. As a consequence, $W_{S,\text{carb}}$ decreased to 500 to 300 kg/m² and $E_{\text{carb}}$ dropped to 40 % (see Fig. 2c).

Stable operation was reestablished at hour 68 (3). The operation with previous conditions was continued except the solid inventory in the carbonator. $E_{\text{carb}}$ was kept at a high level with the lower inventory since $G_{S}$ (see Fig. 2c) and $F_{0}$ (see Fig. 2b) were kept constant. Some fluctuation in the flow of captured CO₂ and consequently in the carbonator efficiency can be observed. Since the CO₂ capture reaction in the carbonator in this period was kinetically controlled, fluctuations in the solid flow entering the carbonator caused fluctuations in the carbonator inventory as well as the flow of captured CO₂ and subsequently in the carbonator absorption rate.

The testing period was finished at hour 85 (4) and a new test point was adjusted. The carbonator was refilled, the incoming CO₂ flow was decreased and the solid circulation rate was increased in order to switch from kinetically to chemical equilibrium controlled absorption in the carbonator. As a side effect, carbonator temperature was slightly increased by the amount of additional solid entering the carbonator. During this period, a very stable operation could be accomplished and only very little fluctuations in the CO₂ flow captured in the carbonator and subsequently in the carbonator absorption efficiency were observed for a period of 20 hours. Minor parameter variations were tested until the end of this operation scenario after hour 110 (5).

An exemplary temperature and pressure profile of the carbonator reactor during this period is shown in Fig. 3b. The hydrodynamic pressure profile indicates the solid distribution in the reactor. A distinct dense zone in the lower part of the reactor is shown by the pressure profile. The dense zone contained most of the inventory whereas only a minor part of the inventory was in the lean zone. In this period, the cooling was accomplished by bayonet cooling tubes in the carbonator to control the average reactor temperature $T_{\text{carb}}$ to 684 °C leading to a volumetric equilibrium concentration $\nu_{\text{CO}_2,\text{carb,eq}}$ of 2.1 %vol. The temperature profile shows a distribution between a warmer dense zone ($T_{\text{carb,dz}}$ = 711 °C) and a colder lean zone ($T_{\text{carb,lz}}$ = 642 °C). In-bed gas analysis show that the main part of the CO₂ is absorbed in the dense zone of the reactor (>80 % of $E_{\text{carb}}$). Equilibrium conditions $\nu_{\text{CO}_2,\text{eq,carbdz}}$ of 3.8 %vol could be achieved in the dense zone. The carbonation reaction runs faster since the higher dense zone temperatures positively affect the reaction kinetics. In order to achieve high carbonator absorption efficiencies, the temperature in the lean zone is lowered by the cooling tubes. There, equilibrium conditions $\nu_{\text{CO}_2,\text{eq,lz}}$ of 0.8 %vol are predominant and carbonation reaction can continue. Approx. 15% of the total carbonator absorption efficiency is realized in the lean zone. All in all following this strategy, high carbonator absorption efficiencies higher than 80 % at equilibrium conditions in the reactor ($\nu_{\text{CO}_2,\text{carb,in}}$ = 2.1 %vol) could be achieved. Equilibrium limited carbonator operation shows a very stable behaviour during the total operating period.
Long-term pilot operation was carried out with various types of fuels. Fuel properties as well as particle sizes were varied. Table 2 provides an overview of the coal used for flue gas production in the furnace as well as providing the required heat for calcination in the calciner reactor. Colombian hard coal was used either in coarse ($d_{50} \sim 1.500 \, \mu m$) or in pulverized ($d_{50} \sim 45 \, \mu m$) particle size in the calciner with a lower heating value (LHV) of 26.5 MJ/kg. Fig. 4 shows the effect of the fuel type and particle size on the sorbent circulating during CaL pilot tests with the same feed ratio of make-up. Obviously, significant difference in the amount of inactive material (gypsum, ash) can be observed depending both on the particle size and on the type of fuel. Using hard coal with the same composition and different particle size distribution, it can be observed that the share of gypsum is similar (~ 10 %$_{\text{mass}}$) and ash differs. With coarse hard coal, 11 %$_{\text{mass}}$ of ash accumulates in the circulating solid stream compared to 5 %$_{\text{mass}}$ firing pulverized coal. The particle size of the coal feed influences the ash separation efficiency in the calciner cyclone. The bigger the ash particles, the more ash is separated and accumulates in the circulating material. A significant difference in gypsum amount can be recognized comparing the composition of the samples for pulverized hard coal as well as lignite. A rather low share of 0.5 %$_{\text{mass}}$ gypsum accumulates in solid circulation firing lignite compared to 10 %$_{\text{mass}}$ with hard coal.

The low sulphur content of the lignite compared to the hard coal (see Table 2) has a positive effect on accumulation of inert material in the process. The sulphur input from the flue gas from the combustor as well as in the calciner firing was lower compared to the hard coal tests.

**CONCLUSION**

The CaL technology is one of the most promising post-combustion CCS technologies. An important step towards the realization of this technology in commercial scale is the successful pilot testing in 1 MW$_{\text{th}}$ scale. Semi-industrial pilot testing of the CaL process during 16 weeks with more than 1,200 hours of stable CO$_2$ capture showed the maturity of the process realizing high CO$_2$ capture rates in steady-state operation. During steady-state operation, CO$_2$ absorption rates in the carbonator higher than 90 % and overall CO$_2$ capture rates higher than 95 % were proven under a wide range of parameters, e.g. fuel characteristics in the calciner, solid circulation rates, make-up rate etc. The calciner fuel particle size and the fuel composition significantly influence the composition of the sorbent circulation between the reactors and thus, its performance to absorb CO$_2$ from the flue gas lead in the carbonator. Enrichment of impurities, meaning ash and sulphur in the circulating solid, are mainly depending on the composition of the coal fueled in the calciner. Increased amounts of impurities represent an inactive fraction decreasing the ability of the sorbent of absorbing CO$_2$. This effect can be compensated by either increased addition of fresh material and extraction of used material or raising the circulating solid stream between the reactors. The data provide the basis for scale up of the CaL technology to a CCS demonstration plant in 20 MW$_{\text{th}}$ scale. Based on the conclusions drawn from operating experience, heat and mass balancing as well as solid analysis are used for design and engineering of a 20 MW$_{\text{th}}$ CaL pilot plant as the next step towards maturity of the technology.

**ACKNOWLEDGEMENTS**

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NOTATION

Abbreviations

- CaL: Calcium Carbonate Looping
- CCS: Carbon Capture and Sequestration
- CFB: Circulating Fluidized Bed
- IGCC: Int. Gasification Combined Cycle
- IHCaL: Indirectly heated CaL
- LHV: Lower Heating Value
- MEA: Mono-Ethyl-Amine

Nomenclature

- $d_{50}$: median particle diameter, μm
- $E_{carb}$: carbonator absorption efficiency
- $E_{total}$: total process capture efficiency
- $F_{CO2,0}$: CO$_2$ flow released from make-up, mol/m$^2$s
- $F_{CO2,carb,out}$: CO$_2$ flow leaving the carbonator, mol/m$^2$s
- $F_{CO2,carb,in}$: CO$_2$ flow entering the carbonator, mol/m$^2$s
- $F_{CO2,calk,out}$: CO$_2$ flow leaving the process, mol/m$^2$s

Greek letters

- $\nu_{CO2,eq}$: CO$_2$ equilibrium (eq.), %vol
- $\nu_{CO2,eq,carb}$: CO$_2$ eq. carbonator, %vol
- $\nu_{CO2,eq,carb,dz}$: CO$_2$ eq. carbonator dense zone, %vol
- $\nu_{CO2,eq,carb,lz}$: CO$_2$ eq. carbonator lean zone, %vol
- $\nu_{CO2,calk,out}$: CO$_2$ concentration carbonator outlet, %vol

REFERENCES


