Characterization of the oxy-fired regenerator at a 10 kW$_{th}$ dual fluidized bed calcium looping facility

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HIGHLIGHTS

- CaL experiments at a 10 kW$_{th}$ DFB system under high CO_2 concentration.
- Performance of the regenerator in terms of calcination efficiency is studied.
- Regenerator efficiency is correlated to reactor geometry and lime properties.
- Lime chemical decay over time is recorded.
- Material losses are measured in realistic CFB conditions.

ARTICLE INFO

ABSTRACT

Calcium looping is a CO_2 capture technology, developed in the last years with great potential to contribute to the reduction of greenhouse gases emissions. It consists of a carbonator where CO_2 contained in power plant flue gas, is absorbed by CaO producing $CaCO_3$ and a regenerator where the $CaCO_3$ is calcined to CaO releasing a highly concentrated CO_2 stream. A key aspect of the process is the oxy-combustion of the fuel in the regenerator to provide the heat for the endothermic calcination reaction. This implies high CO_2 concentration in the off-gas and requires a flue gas recycle. Aim of this work is the characterization of the regenerator operation under this environment and thus experiments were performed at the 10 kW$_{th}$ IFK Dual Fluidized Bed facility. Regenerator efficiency and sorbent performance in terms of chemical activity and mechanical stability are the two basic parameters investigated, while the active space time is used for interpretation of the results. It is found that high calcination conversions can be achieved with temperatures less than 920 °C. Sorbent achieves a residual CO_2 carrying capacity similar to the one referred to the literature. The sorbent proved to be mechanically strong thus optimistic percentage of material loss was recorded to be 0.8 wt.%/h or 0.024 mol Ca/mol CO_2.

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1. Introduction

Carbon dioxide is a major greenhouse gas produced at large quantities from fossil fuel combustion, especially at power plants. The global energy demand in 2040 is expected to be increased by 30% in comparison to 2010, while 40% of energy consumption will be due to electricity generation [1]. This demand will be mostly covered by fossil fuel power plants, while coal-fired power plants are responsible for 33% of the world's CO_2 emissions [1]. Therefore the need for efficient ways of making such power plants environmentally friendly is imperative. This is why the focus has been shifted to extensive research in the development of Carbon Capture and Storage (CCS) technologies, including the calcium looping process.

The calcium looping process, which is already studied for syngas CO_2 removal from the 1960's [2], was firstly proposed by Heesink and Temmink in 1994 [3] as one of the zero emission coal technologies. The general process scheme is shown in Fig. 1 and takes advantage of the reversible carbonation–calcination reaction (1).The process is realized in a dual fluidized bed system (DFB).

$$CaO_{(s)} + CO_{2(g)} \Leftrightarrow CaCO_{3(s)}, \Delta H_{25°C} = \pm 178.2 \text{ kJ/mol} \tag{1}$$

The separation of the CO_2 is done by means of the exothermic carbonation reaction of CaO so that $CaCO_3$ is formed and CO_2 lean

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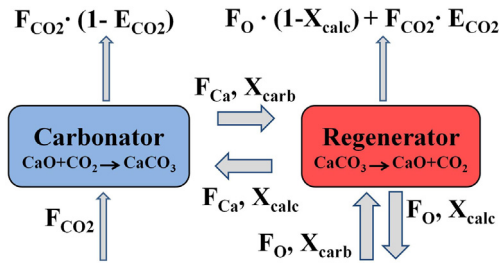*E-mail address:* Glykeria.duelli@ifk.uni-stuttgart.de (G. Duelli (Varela)).

Fig. 1. Calcium looping general process scheme.

gas stream is produced. The regeneration of the CaO makes use of the endothermic calcination reaction and is carried out in the regenerator. In the regenerator coal is burnt under oxy-combustion conditions to drive the high temperature calcination reaction [4]. A CO_2 rich gas stream is produced and after purification is ready for storage. Fresh lime is added continuously to the system to compensate for loss of the material's chemical activity [5], but also for mass losses due to attrition phenomena [6]. The O_2/CO_2 combustion process provides an additional advantage and makes the technology economically competitive [7–10]. Results from bench scale facilities [11–13] as well as from pilot plant tests [14–17] confirm the feasibility of the concept and provide data for the process commercialization.

The investigations performed up to now are mainly focused on the carbonator operation as well as the calcination reaction [18–20] and recently a model for the oxy-fuel combustor/regenerator was proposed [21]. However most of the studies are performed under air-fired conditions thus there is lack of data from a large scale facility where the regenerator is operating under realistic process conditions. For this purpose, IFK performed experiments at a 10 kW_{th} DFB facility investigating the regenerator performance under high CO_2 volumetric concentration as imposed by the oxy-fuel combustion.

2. Theoretical background

The performance of the regenerator is of significant importance for the whole process as it determines the quality and quantity of the sorbent delivered to the carbonator. As it can be seen in Fig. 1, a molar flow of particles (F_{Ca}) with a carbonate content (X_{calc}) is entering the carbonator and after capturing part of the CO_2 (F_{CO_2}) is directed to the regenerator with a carbonate content of X_{carb}. Consequently and by implying simple mass balance equations the amount of CO_2 captured in the carbonator is:

$$F_{CO_2} \cdot E_{CO_2} = F_{Ca} \cdot (X_{carb} - X_{calc}) \tag{2}$$

This equation indicates that higher the carbonate content of the particles exiting the carbonator (X_{carb}) and the lower the carbonate content of the particles entering the carbonator, namely X_{calc}, the lower F_{Ca} will achieve a certain CO_2 capture efficiency. Previous TGA and small lab scale studies report that the high CO_2 concentration in the regenerator where the calcination takes place enhances sintering thus the particles CO_2 carrying capacity (X_{ave}) is reduced [18,22]. It has been found that both the surface area and the porosity of the produced CaO are affected by the presence of CO_2 [22]. Other studies have shown that an increase in the CO_2 partial pressure results in a decrease in the calcination rate [23].

Under these limiting conditions, feeding fresh lime (make-up) in the system can compensate for the loss of sorbent activity by improving the sorbent's carrying capacity. In addition, while high temperatures would ensure full calcination [23], they would also

cause sorbent deactivation as well as ash accumulation resulting in high make-up demands [24,25]. In both cases the heat demands would be increased [26]. Higher residence times would theoretically allow complete calcination but as reported in the literature [24] the average lime CO_2 carrying capacity (X_{ave}) would be decreased due to excessive sintering. Considering these facts the temperature should be kept as low as possible allowed by the thermodynamic equilibrium, in order to decrease the heat demands of the regenerator but also to guarantee high degrees of sorbent calcination conversion.

Several formulas based on different models are proposed by the literature to calculate the calcination reaction rate [23,27,28]. Recent TGA kinetic studies on calcination reaction of Ca based sorbents for calcium looping applications showed that limes follow an apparent homogeneous conversion pattern at particle level [18]. Thus the rate of calcination proposed by Fang et al. [29] based on the grain model by Szekely and Evans [30] is applied as derived from the following equation:

$$r_{calc} = k \cdot \left(1 - \frac{X_{carb} - X_{calc}}{X_{carb}}\right)^{2/3} \cdot (C_{eq.} - C_{CO_2}) \tag{3}$$

In Equation (3) the kinetic constant k ($kmol/m^3$ s) depends on the lime type and the temperature [20]. C_{CO_2} is the concentration of the CO_2 in the reactor and depends on the fuel type as well as the amount of recirculated flue gas. $C_{eq.}$ is the equilibrium CO_2 concentration and is calculated through the Equation (4) below as proposed by Baker [27]:

$$C_{CO_2 eq.} = 4.137 \cdot 10^7 \cdot \exp(-20,474/T) \cdot \rho_g / M_{CO_2} \tag{4}$$

The regenerator efficiency is defined as per Rodríguez et al. [12] and Charitos et al. [19] as the fraction of the calcined particles, where X_{carb} is the carbonate content of particles entering the regenerator and X_{calc} carbonate content of particles exiting the reactor (Fig. 1):

$$E_{reg} = \frac{X_{carb} - X_{calc}}{X_{carb}} \tag{5}$$

As shown in Fig. 1 above a molar flow of particles (F_{Ca}) with a carbonate content of X_{carb} is directed to the regenerator. The two main process parameters that affect the regenerator efficiency [19] are the residence time (t_{res}) and the sorbent's carbonate content (X_{carb}). Assuming that there is no make-up flow to the system, the particle residence time is defined as the ratio of the moles of Ca present in the regenerator and the molar flow of carbonated particles available for calcination:

$$t_{res} = \frac{N_{Ca}}{F_{Ca}} \tag{6}$$

Charitos et al. [19] experimentally observed that the regenerator efficiency increases by decreasing the load of the reactor expressed as the amount of particles to be calcined in a certain time. This load is formulated as follows:

$$L_{reg} = \frac{X_{carb}}{t_{res}} \tag{7}$$

Moreover, the reaction rate is considered constant until it reaches a critical time t_c after which it becomes zero (Equation (8)). This means that only the fraction of particles with a residence time less than the critical time is available for calcination (f_a). This concept is proposed by Martinez et al. [20]. The critical time is calculated using Equation (9) which results from integration of the Equation (3) for $X_{calc} = 0$. Finally assuming the fluidized bed