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Operation of a 300 kW_{th} Indirectly Heated Carbonate Looping Pilot Plant for CO_2 Capture from Lime Industry

Carina Hofmann[1], Martin Greco-Coppi[1], Jochen Ströhle[1], Bernd Epple[1]

[1] *Technical University of Darmstadt, Institute for Energy Systems and Technology, 64206 Darmstadt, Germany*

Corresponding Author: Jochen Ströhle, jochen.stroehle@est.tu-darmstadt.de

Abstract

The indirectly heated carbonate looping (IHCaL) process is a novel technology for capturing CO_2 from the lime and cement industry. The IHCaL process uses lime as solid sorbent, which comprises synergies with lime and cement plants using same solid materials. Another major advantage of the IHCaL process is the high energetic efficiency. Previous pilot tests proved the feasibility of the IHCaL process for applications in the power plant sector. However, the integration of the IHCaL into cement and lime plants, as well as the usability of spent sorbents as educts in such productions, has not yet been tested. This study describes the design and operation of an existing 300 kW_{th} pilot plant that is adapted for demonstrating the IHCaL process under industrially relevant conditions of lime plants. First results show that the fluidized bed reactor system can be operated under stable conditions and high CO_2 capture rates can be achieved when the temperature and solid inventory in the carbonator are high enough.

Keywords: Carbonate looping, Fluidized bed conversion, Heat pipes, Lime production, Solid looping, Pilot plant, Indirect heating

1. Introduction

The production of lime and cement accounts for around 8 % of anthropogenic CO_2 emissions [1]. These emissions are classified in two categories according to their source: unavoidable process CO_2 emissions caused by calcination of the raw educts, e.g. natural limestone, and CO_2 emissions resulting from the combustion of fuels to generate the necessary heat for the endothermic calcination. While renewable fuels can be utilized to reduce CO_2 emissions from combustion, the process CO_2 emissions account for around 65% of emissions and can only be avoided by CO_2 capture [2]. Several CO_2 capture technologies are currently being developed to address this problem.

The carbonate looping (CaL) process has the potential to significantly reduce the efficiency loss compared to solvent-based technologies, since the process operates at high temperatures, which allows for the utilization of heat for power production in a highly efficient steam cycle [3]. The CO_2 contained in the flue gas of an industrial plant is absorbed by CaO in the carbonator at around 650 °C. The $CaCO_3$ formed hereby is transferred to the calciner, where the CO_2 is released by an increase of temperature to around 900 °C. The stream of highly concentrated CO_2 is ready for compression and storage/usage, and the regenerated CaO is transferred back to the calciner closing the solid loop. Since the calcination reaction is endothermic, the calciner needs to be supplied with heat. The most straightforward approach to deliver the heat for calcination is via oxy-combustion in the calciner. This technology has been proven in several test rigs up to 1.7 MW_{th} for processing flue gas from coal-fired power plants [4, 5]. The technology has been proven for artificial cement kiln flue gases at the 30-200 kW_{th} scale [6, 7].

The CaL process can be further improved if the need of oxygen and thus an air separation unit (ASU) can be avoided [8]. This can be realized by indirect heating of the calciner from an external combustion chamber, e.g. via heat pipes. In the heat pipes, a liquid, e.g. sodium, evaporates and condensates providing an optimal heat transfer performance [9]. The flue gas generated in the external combustion

chamber is directed to the carbonator, where most of the CO_2 contained in this flue gas reacts with CaO. A schematic of such a process is given in Figure 1. Besides low energy penalty and high potential for integration, the indirectly heated carbonate looping (IHCaL) process gives the possibility to combine the CO_2 capture with the utilization of fuels with a high biogenic fraction. This concept can lead to net negative CO_2 emissions [10]. The IHCaL process offers further advantages. An almost pure CO_2 stream is obtained after the calciner minimizing the efforts for CO_2 purification. Practically no impurities (e.g. ash) are present in the system, thus reducing the amount of inert mass that has to be heated up each cycle and increasing the purity of the used sorbents. The mild calcination conditions lead to a low sorbent deactivation, low fragmentation, and low attrition rates of the particles, which reduces the make-up requirements and thereby increases the efficiency of the process [8].

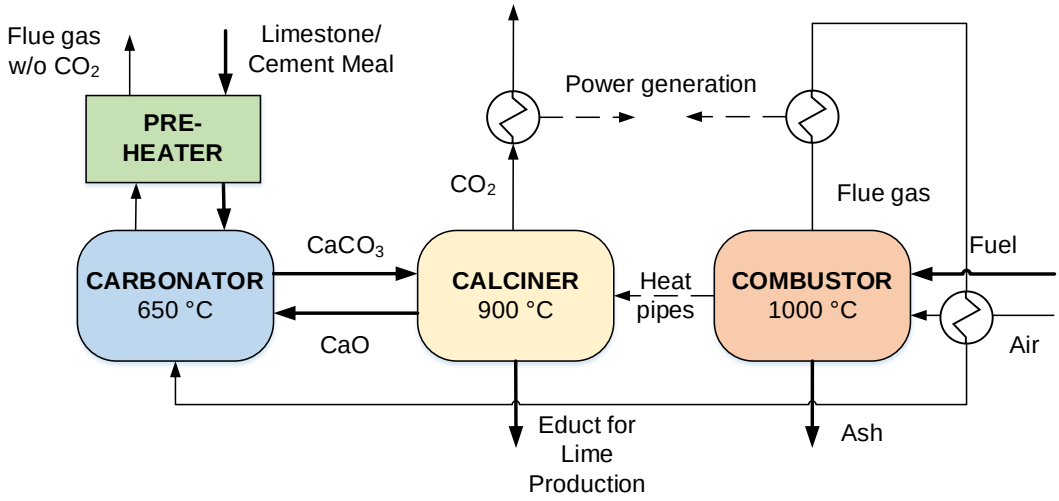

Figure 1. Schematic of the integration of the IHCaL process into lime-based production processes

Greco-Coppi et al. [11] showed that the IHCaL process has a high potential to decarbonize the lime industry by reducing direct CO_2 emissions by up to 87 %. They considered two options for integrating the carbon capture technology, a tail-end integration, in which an additional system for the flue gas handling is installed downstream of the kiln, and a full integration, in which a complete new lime burning system is implemented, where the IHCaL reactor system replaces the kiln.

The IHCaL process with three fluidized bed reactors was previously tested with regard to CO_2 capture from coal-fired power plants [12]. The 300 kW_{th} pilot plant at Technical University of Darmstadt was operated successfully over 400 hours, capturing CO_2 from an artificial flue gas. This facility is unique worldwide. So far, the IHCaL process has only been tested for power plant applications [8, 12], but not for lime or cement plants. Therefore, the existing 300 kW_{th} IHCaL test facility has been modified for operation and investigation of the IHCaL process under the conditions of an integration into cement and lime plants. Furthermore, the assessment of the sorbent usage as further product in these processes is foreseen as part of the imminent research campaigns [13]. In the present work, the design modifications and commissioning of the pilot plant at lime plant conditions are presented. Finally, first operational results from the first test campaign are presented.

2. Experimental

2.1. The 300 kW_{th} pilot plant

The heart of the 300 kW_{th} pilot plant consists of three fluidized bed reactors, as shown in Figure 2. The carbonator is designed as a circulating fluidized bed (CFB) reactor (1), while the calciner operates as a bubbling fluidized bed (BFB) reactor (2). Several coupling devices interconnect both reactors. A cone valve between carbonator and calciner (3) controls the global solid circulation. The combustor (4) is designed similarly to the calciner, being fueled and thermally connected with the calciner via 72 heat pipes. The main parameters of the reactors are indicated in Table 1. Besides the core components,

several peripheral components are included in the test rig. The flue gas of each reactor is cooled down and mixed together before entering the stack. All reactors can be fluidized with preheated fluidization agents, with a temperature up to 550°C. A detailed description of the existing pilot plant is given by Reitz et al. [9].

The pilot plant is modified in order to demonstrate the feasibility of the process under industrially relevant conditions, i.e. using the same fuels, sorbents, and operating parameters as expected in large-scale commercial IHCaL plants for lime and cement applications. Therefore, the combustor is complemented with a solid fuel feeding system in order to be fueled with coal or waste-derived fuels. Furthermore, as a means to supply the carbonator with real flue gas, the combustor and carbonator are connected by a new duct to direct the combustor off-gas to the carbonator. A simplified process flow diagram of the IHCaL pilot plant is shown in Figure 3, including the major upgrades in red. Hofmann et al. [14]give a more detailed explanation and description of the modifications performed.

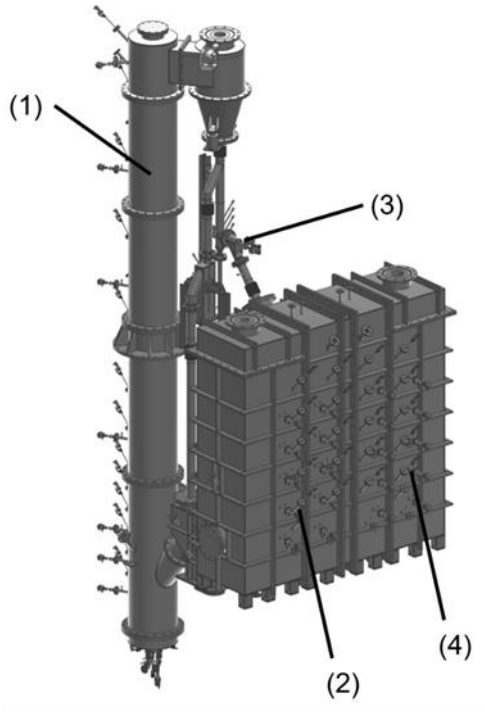

Figure 2. IHCaL reactor system with main components

Table 1. Reactor parameters of the 300 kW_{th} IHCaL pilot plant

Parameter	Unit	Carbonator	Calciner	Combustor
Height H	m	8.00	2.6	2.6
Inner Diameter / L x W	m	⌀ 0.25	1.1 x 0.3	1.1 x 0.3
Outer Diameter / L x W	m	⌀ 0.6	1.4 x 0.9	1.4 x 0.9
Temperature	°C	650	900	1000

2.2. Modifications of the pilot plant

Figure 3 shows a simplified configuration of the 300 kW_{th} IHCaL test facility including the major adaptions in red. These adaptions are briefly explained below. The modifications are implemented into the pilot plant in two steps: first the flue gas circulation and sorbent dosing, purging & sampling, then the solid feeding and steam fluidization.

2.2.1. Flue gas circulation

The flue gas composition after the combustor is measured by an on-line gas analysis. Downstream, the flue gas is cooled down to approximately 180°C in a water-cooled heat exchanger, preventing the flue gas from falling below the dew point of sulfuric acid. The cooler has a capacity of 120 kW_{th}. The flue gases are dedusted in a bag filter to protect the downstream equipment and allow for the utilization of the flue gases as fluidization agent in the carbonator. After the filter, a portion of the cooled and dedusted flue gas can be introduced directly into the flue gas handling system of the test rig. The flow of flue gas into the carbonator is controlled via a motorized flap. Two radial fans in series are installed in order to deliver and control the pressure level for fluidization of the carbonator via the three fluidization nozzles (Δp= 350 mbar). Before entering the carbonator, the volume flow is measured by means of an orifice plate. CO_2 from tanks, electrically preheated, can be mixed into this stream. The CO_2 stream is controlled via a mass flow controller.

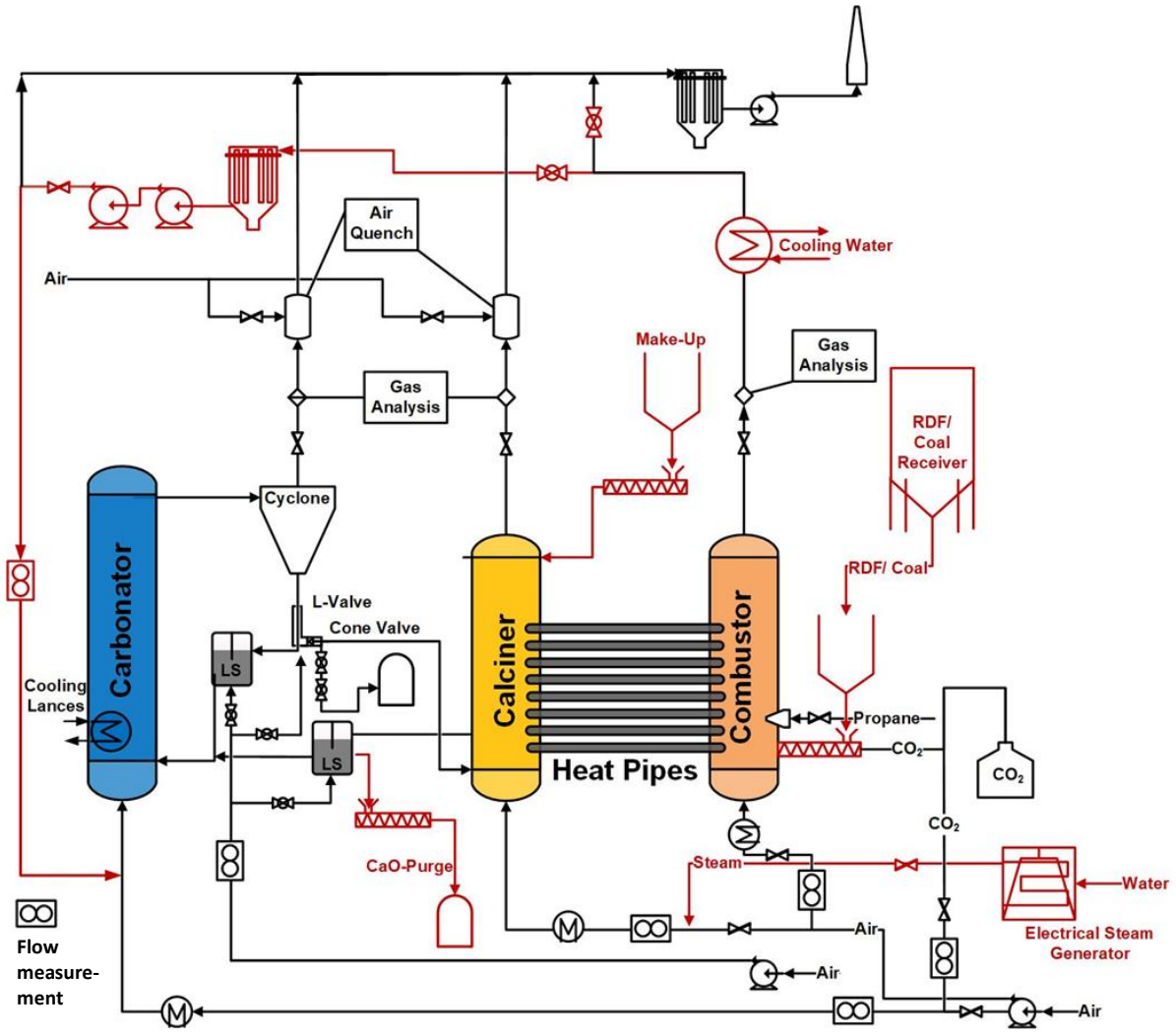

Figure 3. Schematic of the IHCaL 300kW$_{th}$ pilot plant implementing the adaptions

2.2.2.Sorbent dosing, purging and sampling

For continuous dosing and discharging of deactivated material, two additional components are installed. The reactor system is equipped with two entry points for fresh material ($CaCO_3$), one in the upper part of the calciner and the other one in the lower part of the carbonator. The port at the calciner is preferably used as it has a smaller impact on the heat balance of the reactor system. The fresh material is continuously fed via a loss-in-weight feeder into the calciner. Besides the existing sampling of $CaCO_3$ after the carbonator, a frequency-controlled extraction screw conveyor is implemented into the loop seal after the calciner. This allows for a continuous purging of up to 20 kg/h solid material. The hot material is cooled down and collected in a vessel made of high temperature steal. This vessel is periodically replaceable and samples can be taken for off-line analysis. These samples enable the determination of the phase composition after each reactor and improve the balancing of the system. Especially, the off-line analysis of the burnt sorbent (CaO) gives important insights into the calcination degree and its potential to be used in cement or lime products.

2.2.3. Solid feeding

Previously, the pilot plant was fueled with propane. To enable industrially relevant conditions, the BFB reactor is modified with a solid feeding system. The solid feedstock enters the system from a container. This container discontinuously feeds into a weighed container. The solid flow from the weighed container into the combustor is controlled via a screw conveyor. An additional water-cooled screw feeder introduces the material directly into the lower part of the bubbling bed of the combustor. To avoid

backflow of gases from the reactor and to ensure the feeding, the weighed container is pressurized with CO_2 to the bed pressure, and a rotary valve is installed before the cooled screw.

2.2.4. Fluidization

Each reactor is equipped with an electrical preheating system for its fluidization agent with a capacity of 35 kW (max 550 °C). In previous operation, the calciner was fluidized with air to support the self-fluidization effect of the released CO_2. Air is used for simplification. It reduces the partial pressure of CO_2 and consequently lowers the calcination temperature. With an air mass flow of 50 kg/h, the minimum temperature for calcination is around 850 °C, calculated with a correlation from Garcia-Labiano [15]. This temperature is close to the average temperature in the calciner from previous results (i.e. 830 °C). Technically, it is not feasible to use air in the calciner, since it dilutes the pure CO_2 stream leaving the system. In future tests, steam will be used as fluidization agent instead of air, since it has the same effect of decreasing the partial pressure of CO_2. Consequently, the application comes closer to real industrial application, and the effect of steam on the calcination can be assessed at pilot scale. The steam is generated in an electrical steam generator; approximately 30 kg/h are necessary. The flow is controlled via a magnetic valve and measured with an orifice plate. Before entering the calciner, the steam is heated up to a temperature of max. 550 °C.

2.3. Operating Conditions

Three different test campaigns are planned with varying combinations of solid feedstock and operating conditions. The main design parameters of the test facility for corresponding pilot test are listed in Table 2. During the first test campaign, the flue gas circulation is commissioned and general operational experience is collected. The combustor is fuelled with propane. Fluidization agent of the calciner and combustor is air, while the carbonator is fluidized with flue gas from the combustor. Limestone with a particle size distribution of 100 – 300 µm is used as the sorbent. For optimal operation, the dimensionless superficial velocities of the reactors should be in the ranges depicted in Figure 4. Taking the self-fluidization in the calciner into account [16], this results in a rather low gas velocity at the calciner inlet. One target of the pilot tests is to produce calcined material to be analysed regarding the further utilization in any kind of lime-based product or compound for cement clinker, fulfilling the quality requirements.

Table 2. Test Facility design parameters for first pilot test

Parameter	Unit	Carbonator	Calciner	Combustor
Temperature	°C	600 - 700	750 - 950	850 - 1050
Fuel	-	-	-	propane
Thermal power	kW_{th}	-70 by cooling lances	0 – 190 by heat pipes	150 – 300 by fuel
Fluid preheat temperature	°C	100 - 250	100 - 550	100 - 550
Fluidization agent	-	flue gas + CO_2	air	air
Fluidization gas velocity	m/s	3.5	0.3	1.55
Bed material	-	$CaO/CaCO_3$	$CaO/CaCO_3$	Sand
Solids inventory	kg	30 - 60	350 - 450	500 - 650
Particle size	µm	100 - 300	100 - 300	500 - 1000

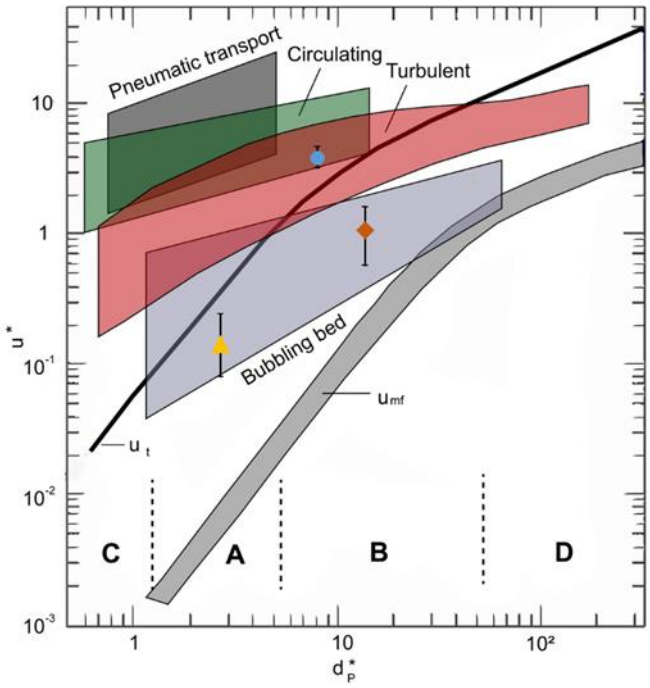

Figure 4. Grace diagram indicating the operating regimes for the calciner ▲, carbonator ●, and combustor ♦ [17]

3. Results and Discussion

In a first step, the flue gas system connecting combustor and carbonator was commissioned in January 2022. The pilot plant was in operation for more than 150 h and a stable operation was achieved. In this work, first results of stable operating points with an artificial flue gas mixture of air and CO_2 are presented.

3.1. Pressure and temperature profile

The modifications of the existing pilot plant influence the hydrodynamics. This behaviour has been studied in order to ensure the operability of the system. Figure 6 shows a typical pressure profile of the pilot plant. Figure 5 indicates the position of the measurements. The operational behaviour of the reactor system as well as the material balance between the reactors appear to be stable. A sufficient make-up flow to the system compensates losses through the cyclones. Even with low pressure at the L-valve (1d, 1c), the material transport between the reactors works well, as long as the pressures of the reactors itself are adjusted accordingly (pressure difference 2a,1c). Furthermore, all other coupling devices showed good operability (1e,2c). By the constant filling level of the standpipe, caused by the overflow of material to the internal recirculation of the carbonator (1e), well-defined pressure profiles are achieved all the time. The solid flux between the reactors is either controlled by the cone valve or the fluidization velocities in the carbonator. The second served as control during the indicated set point. It is observed that, even with low gas velocities (~2.5 m/s), sufficiently large solid fluxes between the reactors could be achieved.

In Figure 7, the corresponding temperature profile is shown. The temperature profile in the bubbling bed of both, calciner and combustor, is very homogeneous. There are slightly higher temperatures in the bed region than in the free-board, which indicates complete combustion in the bed zone. Besides this, a homogeneous temperature in the carbonator reveals a good mixture of solids and gas, as well as enough solid inventory and sufficient fluidization. The low temperature in the loop seal of internal recirculation is caused by a low solid internal flux.

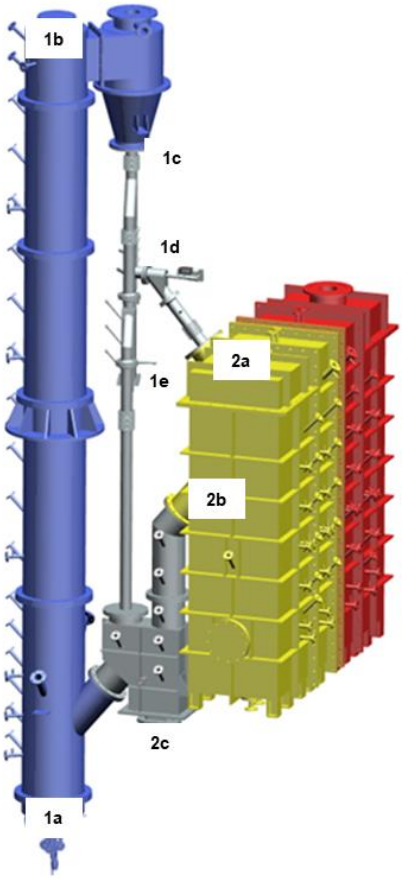

Figure 5. Pressure profile of the IHCaL pilot plant

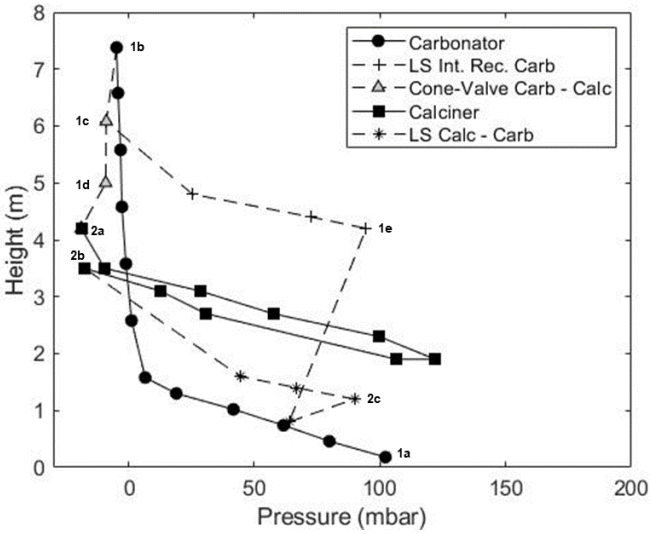

Figure 6. Pressure profile of the IHCaL pilot plant

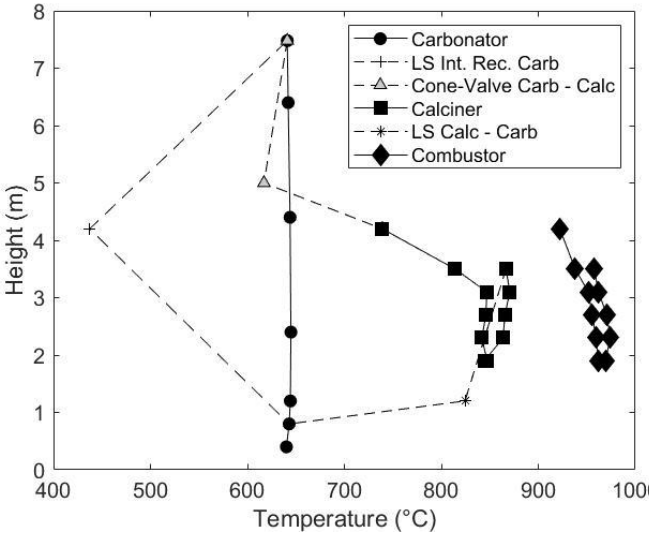

Figure 7. Temperature profile of the IHCaL pilot plant

3.2. Carbonator CO_2 capture efficiency

The CO_2 capture efficiency in the carbonator, E_{Carb}, is defined as the amount of CO_2 captured with respect to the CO_2 supplied to the reactor and can be calculated as follows:

$$E_{Carb} = \frac{F_{CO_2,in} - F_{CO_2,out}}{F_{CO_2,in}} \quad (1)$$

With $F_{CO_2,in}$ and $F_{CO_2,out}$ being the inlet and outlet molar flow rates of CO_2 at the carbonator. The carbonator CO_2 capture efficiency for two steady-state operating points of the first test campaign as a function of the temperature and pressure drop in the carbonator is depicted in Figure 8. These operating points exhibit conditions with high inventory (Cluster #1) and moderate inventory (Cluster #2). There is a correlation between bed inventory, which is proportional to the pressure drop across the bed, and the CO_2 capture efficiency. This effect disappears when there is enough active material in the reactors, as discussed in Reitz et al. [12]. Furthermore, there is a direct effect of the temperature on the efficiency at low pressure drop, which has been observed by Reitz et al. [12]. This trend can be explained by the fact that at low pressure drop across the bed, there is a low amount of active material available in the reactor, so that the conversion is limited by reaction kinetics. This means that the reaction rate increases with increasing temperature, as long as the temperature is so low that the reaction is not limited by the

chemical equilibrium. A capture efficiency of up to 85% was achieved with artificial flue gas without steam. A preliminary evaluation of set points with real flue gas showed even higher capture rates.

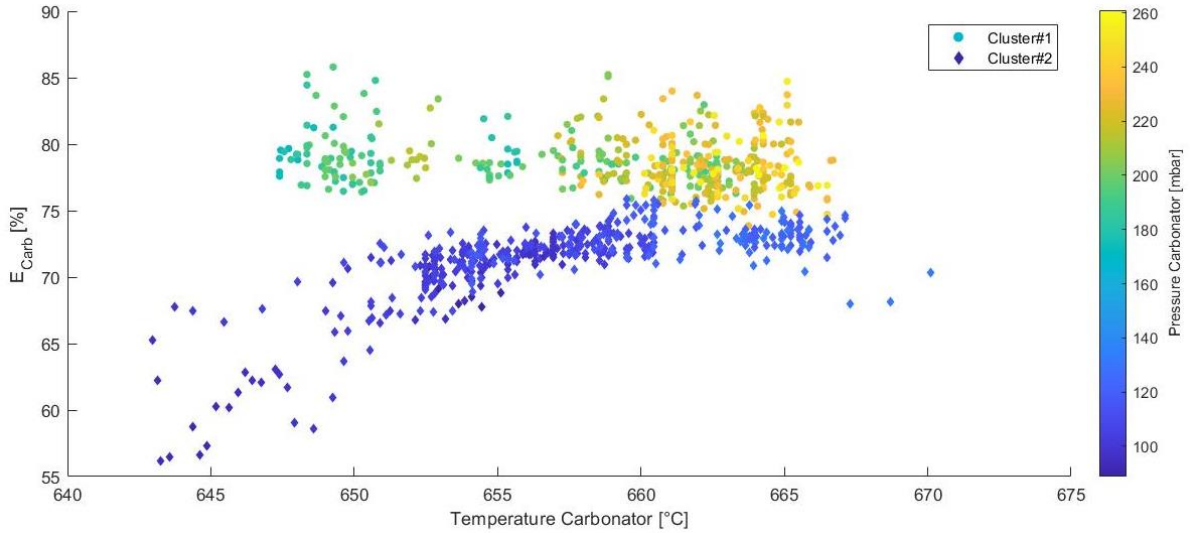

Figure 8. CO_2 capture efficiency of the carbonator for two stable operating points, one at high inventory (Cluster #1) and another at low inventory (Cluster #2), with artificial flue gas as a function of the temperature and pressure drop in the carbonator

4. Conclusion

A 300 kW_{th} IHCaL pilot plant has been adapted to realize industrially relevant conditions for applications to lime and cement plants. The flue gas circulation system has been successfully commissioned, and first stable operating points have been achieved with carbonator CO_2 capture rates over 85%. Further steps are the evaluation of the collected data and the analysis of the sorbent samples that have been taken during the test campaign. Two test campaigns will follow to test the feeding of the combustor with solid feedstock, to use of different sorbents such as cement raw meal, and to improve the CO_2 capture efficiency by optimizing the operating conditions.

5. Acknowledgment

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