Fuel xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

Long-term pilot testing of the carbonate looping process in 1 MW_{th} scale

Jochen Hilz*, Martin Helbig, Martin Haaf, Alexander Daikeler, Jochen Ströhle, Bernd Epple

Institute for Energy Systems and Technology, Technische Universität Darmstadt, Otto-Berndt-Str. 2, 64287 Darmstadt, Germany

ARTICLE INFO

Keywords:
Calcium looping
CO_2 capture
Pilot plant
Dual fluidized bed
Oxy-fuel regenerator

ABSTRACT

The carbonate looping (CaL) process is an efficient post-combustion carbon capture technology to reduce the amount of CO_2 released by fossil fuelled power and industrial plants. This work presents the results gained in long-term pilot tests performed in a 1 MW_{th} CaL pilot plant at Technische Universität Darmstadt. The experimental data were obtained from continuous operation under realistic CaL process conditions, i.e. coal originated flue gas from a coal fired furnace to be decarbonized in the carbonator and oxy-fuel conditions in the calciner. Steady-state conditions, achieved while parameters were not changed during periods up to 60 h, delivered reliable experimental data to scale up the CaL process to industrial size. The feasibility of the CaL process in semi-industrial size was proven by steady-state CO_2 absorption for more than 1200 h with absorption rates in the carbonator higher than 90% and overall capture rates higher than 95% under a wide range of operating parameters, e.g. type of fuel, flue gas composition or reactor temperatures. Exemplary operation to achieve steady-state conditions is presented to show the evolution of the carbonator absorption efficiency and solid properties, such as conversion from CaO to $CaCO_3$ by carbonation and to $CaSO_4$ by sulphation. The carbonator performance was assessed by reasonably closing the carbon balances and applying the active space time as a key parameter to interpret the trends observed.

1. Introduction

Carbonate looping or calcium looping (CaL) is an efficient post-combustion CO_2 capture technology using limestone based sorbents, and which was initially proposed by Shimizu et al. [1]. CaL is particularly suited for retrofitting existing power plants. As shown in Fig. 1, the CO_2 contained in the flue gas from an emission source, e.g. an upstream power plant, is absorbed by calcium oxide (CaO) in the carbonator in an exothermic reaction at around 650 °C forming calcium carbonate ($CaCO_3$) according to Eq. (1).

$$CaO_{(s)} + CO_{2(g)} \leftrightarrow CaCO_{3(s)} + 178.2\ kJmol^{-1} \quad (1)$$

The $CaCO_3$ is transferred to the calciner. By increasing the temperature up to around 900 °C, the CO_2, bound in the solid phase, is released in the endothermic backward reaction according to Eq. (1). A gas stream of highly concentrated CO_2 leaves the calciner, while the CaO is returned to the carbonator. In the basic concept, i.e. the directly heated or oxy-fired CaL process, the heat for the endothermic calcination reaction is provided by oxy-fuel combustion of fuel (e.g. coal) with oxygen from an air separation unit (ASU). Various concepts of optimized CaL processes have been proposed utilizing indirect heat transfer from a combustor to the calciner [2–4]. A very promising approach for the indirectly heated CaL process (IHCaL) heat pipes has recently been tested [5].

The CaL technology promises substantial abatement in energy penalty [6–8] and costs [9–11] compared to other CO_2 capture technologies, e.g. amine scrubbing (post-combustion), integrated gasification combined cycle (pre-combustion) or oxy-fuel combustion. CaL is the only CO_2 post-combustion technology offering additional power generation from the additional heat input required for the sorbent regeneration since the calciner adds an oxy-fired new power plant system to the existing upstream plant. Both carbonation and calcination reactions run at very high temperatures allowing a highly efficient heat recovery from different sources offered by the CaL process.

The oxy-fired CaL process passed through a rapid development of the Technology Readiness Level (TRL) [12] from concept (TRL2) to demonstration at industrially relevant environment (TRL6) [13]. A system consisting of two interconnected circulating fluidized bed (CFB) reactors, a carbonator and a calciner, is the most developed CaL configuration. Synergies between CaL and existing CFB reactor systems at industrial scale promoted the rapid development of this technology during the last decade. Several research groups worldwide

Abbreviations: ASU, Air separation unit; CaL, Calcium/carbonate looping; CFB, Circulating fluidized bed; IHCaL, Indirectly heated carbonate looping process; LHV, Lower heating value; PSD, Particle size distribution; TGA, Thermogravimetric analysis; XRF, X-ray fluorescence

* Corresponding author.
E-mail address: jochen.hilz@est.tu-darmstadt.de (J. Hilz).

http://dx.doi.org/10.1016/j.fuel.2017.08.105
Received 1 May 2017; Received in revised form 11 August 2017; Accepted 29 August 2017
0016-2361/ © 2017 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/BY-NC-ND/4.0/).

Nomenclature

d_{50}	median particle diameter (μm)
$(dX/dt)_{carb}$	carbonation reaction rate (1/s)
E_{carb}	carbonator absorption efficiency (%)
$E_{carb,eq}$	maximum carbonator absorption efficiency at equilibrium conditions (%)
F_0	molar make-up flow (mol/m^{2}s)
f_{active}	active particle fraction of carbonator inventory (−)
$F_{CO2,carb,in}$	molar flow of CO_2 entering the carbonator (mol/m^{2}s)
$F_{CO2,carb,out}$	molar flow of CO_2 leaving the carbonator (mol/m^{2}s)
G_s	solid circulation flow between reactors (kg/m^{2}s)
k_s	reaction rate constant (1/s)
LR	sorbent looping ratio (mol_{Ca}/mol_{CO2})
M_{Ca}	weighted molar weight of Ca particles (g/mol)
MR	make-up ratio (mol_{Ca}/mol_{CO2})
$n_{Ca,carb}$	Ca inventory in carbonator (mol/m^2)
$n_{Ca,carb,active}$	active Ca inventory in carbonator (mol/m^2)
t^*	time required to increase the carbonate content from X_{calc} to X_{ave} (s)
T_{calc}	average calciner temperature (°C)
T_{carb}	average carbonator temperature (°C)
T_{carb}	average carbonator temperature (°C)
$W_{s,carb}$	total carbonator inventory (kg/m^2)
X_{ave}	average CO_2 carrying capacity (mol_{CaCO3}/mol_{Ca})
X_{calc}	molar carbonate content of sorbent leaving the calciner (mol_{CaCO3}/mol_{Ca})
X_{carb}	molar carbonate content of sorbent leaving the carbonator (mol_{CaCO3}/mol_{Ca})
$X_{sulphur}$	molar sulphur content of the sorbent (mol_S/mol_{Ca})
y_{CaO}	CaO mass fraction of the sorbent (wt.%)
y_{CaCO3}	$CaCO_3$ mass fraction of the sorbent (wt.%)
y_{CaSO4}	$CaSO_4$ mass fraction of the sorbent (wt.%)
y_{ash}	ash mass fraction of the sorbent (wt.%)
$\nu_{CO2,calc,in}$	inlet calciner volumetric CO_2 fraction (vol.%)
$\overline{\nu_{CO2,carb}}$	average carbonator volumetric CO_2 fraction (vol.%)
$\nu_{CO2,carb,eq}$	equilibrium carbonator volumetric CO_2 fraction (vol.%)
$\nu_{CO2,carb,in}$	inlet carbonator volumetric CO_2 fraction (vol.%)
$\nu_{CO2,carb,out}$	outlet carbonator volumetric CO_2 fraction (vol.%)
$\nu_{CO2,eq}$	equilibrium volumetric CO_2 fraction (vol.%)
$\nu_{H2O,calc,in}$	inlet calciner volumetric H_2O fraction (vol.%)
$\nu_{O2,calc,in}$	inlet calciner volumetric O_2 fraction (vol.%)
τ_{active}	active space time (s)
φ	gas–solid contacting effectivity factor (−)
φk_s	apparent carbonation rate constant (1/s)

demonstrated the feasibility of the CaL process. Various pilot plants in sufficient scale and with different reactor configuration and capacities were built and operated, e.g. the 0.2 MW_{th} pilot in Stuttgart [14], the 1 MW_{th} pilot in Darmstadt [15], the 1.7 MW_{th} pilot in La Pereda [16] or the 1.9 MW_{th} pilot in Taiwan [17].

As indicated before, the development of the CaL technology achieved a great progress confirming the feasibility of the technology. Nevertheless, a challenge of the CaL technology is a decreasing reactivity with increasing number of cycles of carbonation and calcination [18]. To diminish this effect, a continuous feed of limestone as make-up is required in order to maintain a certain capacity of the sorbent to absorb CO_2 [19]. Consequently, a realistic assessment of sorbent performance can only be provided by a homogeneous mixing of existing and continuous make-up feed. Therefore, extensive long-term operating is required to achieve steady conditions of the sorbent phase.

In addition, the carbonation/calcination reaction is dependent on the CO_2 partial pressure. The oxy-fuel combustion in the calciner implies calcination conditions under high CO_2 concentrations and the presence of water vapour. Various investigations [20–22] pointed out that CO_2 partial pressure and water vapour significantly influence the calcination of the sorbent. Realistic operating conditions can only be achieved by recirculating flue gas instead of mixing artificial calciner primary gas consisting of O_2 and CO_2.

To overcome the uncertainties of previous pilot tests as a basis for scale-up scenarios, the long-term operation under realistic process conditions, e.g. homogeneous mixing of inventory and make as well as oxy-calcination under flue gas recirculation, is required to obtain the confidence about the performance of the CaL technology. Therefore, extensive pilot tests in an upgraded pilot plant at Technische Universität Darmstadt were performed to take the next step towards maturity of the technology addressing the challenges mentioned before. The achievement of steady-state operation has recently been shown by Helbig et al. [23]. This approach guarantees a solid ground for the scale-up of a 20 MW_{th} pilot plant designed and engineered applying the experimental data from long-term pilot tests.

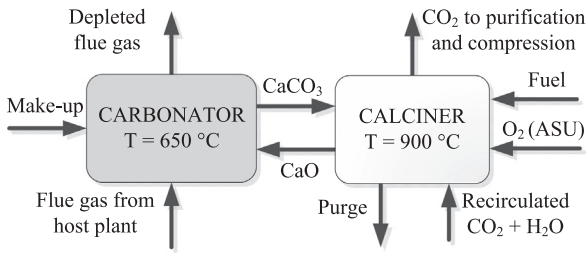


Fig. 1. Principle of the carbonate looping process.

This paper contributes to the progress in the development of the CaL post-combustion CO_2 capture technology. The results obtained from long-term pilot testing in the CaL pilot plant at Technische Universität Darmstadt are presented focusing on the closure of the carbon balance during continuous pilot operation taking into account two out of four test campaigns. Thereby, different types of fuels as well as fuel with various particle size distributions were fired in the calciner. A modelling approach successfully applied in small scale experiments [24–26] is used to interpret the experimental results.

2. Experimental

2.1. Pilot plant setup

A semi-industrial scale CaL pilot plant consisting of two interconnected CFB reactors and a combustion chamber with a thermal capacity of 1 MW_{th} each is located at Technische Universität Darmstadt. In previous tests [15,27], the main focus was proof of operation in 1 MW_{th} scale. Therefore, CaL tests were accomplished decarbonizing synthetic flue gas, a mixture of air and CO_2. The calciner was operated with oxygen enriched air in these tests not representing realistic operating conditions in terms of calcination. As a consequence from these results, the pilot plant was upgraded to operate with coal originated flue gas from the furnace and oxy-combustion in the calciner.

The scheme of upgraded 1 MW_{th} CaL pilot plant is shown in Fig. 2. The CaL reactor systems consists of a carbonator with an inner diameter of 0.6 m and a height of 8.6 m. The dimensions of the calciner are 0.4 m and 11 m, respectively. Both reactor loops include high efficiency cyclones separating the particles from the decarbonized flue gas and CO_2 rich stream leaving the carbonator and the calciner, respectively. The separated solids fall down in loop seals where a part is internally recirculated or transferred to the other reactor (from carbonator to calciner and vice versa). Both reactors are equipped with all conventional

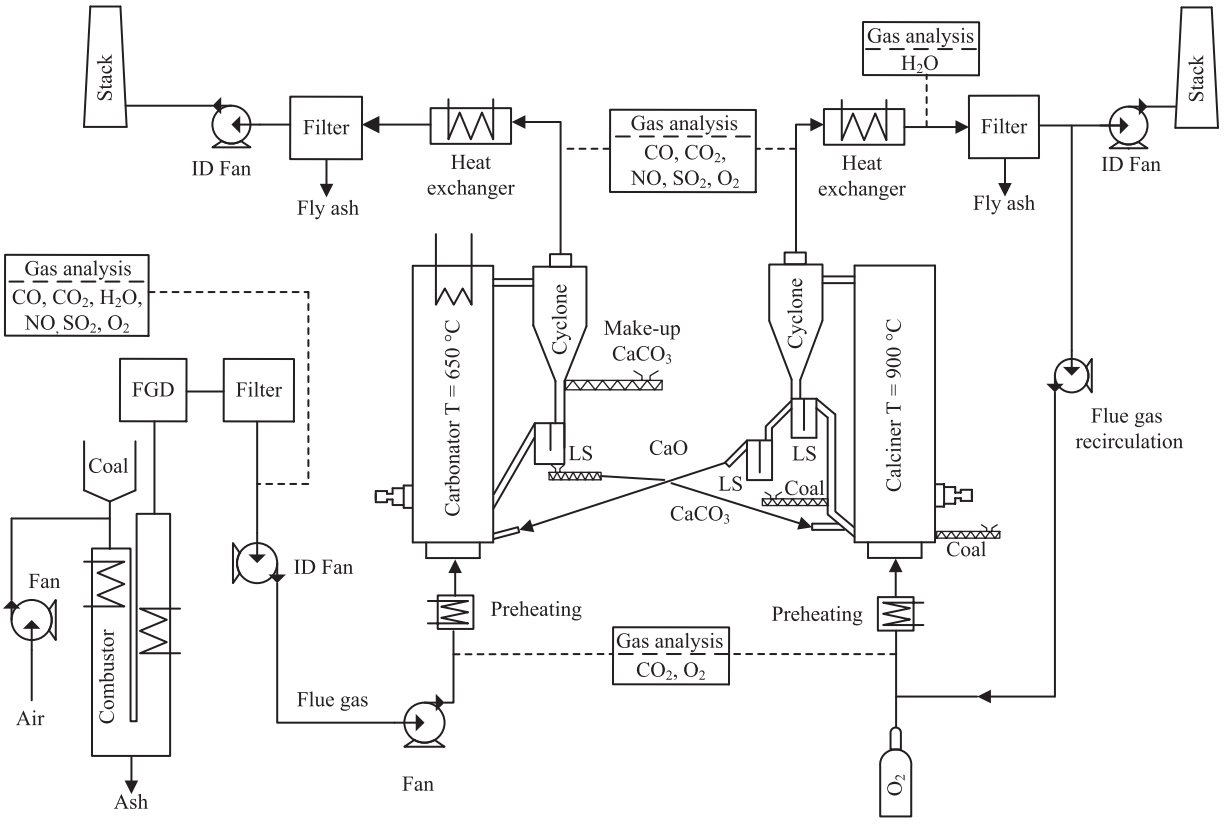


Fig. 2. Scheme of the 1 MW_{th} CaL pilot plant.

components of industrial CFB systems, i.e. refractory lining, start-up burners fired by propane, two-pass heat exchangers to cool down the off-gases, bag filters to remove entrained solid particles, water-cooled screw conveyors to extract solids. Additionally, the carbonator is equipped with five axially arranged internal cooling tubes. The cooling tubes allow the extraction of released heat in the exothermic carbonation reaction to operate at various reactor temperatures. The carbonator flue gas is provided by the combustion chamber and is fed to the reactor with a fan. Sorbent is continuously fed as make-up to the carbonator by a gravimetric dosing system. The calciner is operable under air and oxy-fuel combustion conditions. Coal is continuously fed by a gravimetric coal dosing system either in the return leg or in the bottom of the calciner. Different types of coal, i.e. hard coal or lignite, in various particle size fractions from pulverized to coarse, can be fed to the system. For start-up, air combustion is used to heat up the reactor. Oxy-firing is applied in regular CaL operation. Therefore, liquefied oxygen provided by a tank storage is diluted with recirculated flue gas, coming from the cyclone after cooling and filtration. The solid mass flow from carbonator to calciner is controlled by a screw conveyor. The solid mass flow vice versa is balanced by the entrainment in the calciner reactor, controlled by the fluidization velocity. The calciner reactor was operated in once through without internal recirculation.

The plant setup is equipped with comprehensive instrumentation. Temperature, pressure, flow and continuous online gas measurements are installed at all relevant spots. Ports in the reactors provide the possibility to conduct in-bed measurements of flow patterns, i.e. particle concentration and velocity, and gas concentrations at various heights. In addition, sampling ports allow to extract material from the loop seals and reactors as well as from the heat exchangers and filters. The solid samples extracted are subsequently analyzed in terms of chemical composition, CO_2 carrying capacity and particle size distribution (PSD) by X-ray fluorescence (XRF), thermogravimetric analysis (TGA), a small batch fluidized bed reactor and an air jet sieve.

The present work focuses on the evaluation of the results from long-term pilot testing, i.e. periods of at least 20 h up to 60 h in steady operation. The reliable assessment of CaL sorbent performance demands for steady-state process operation, i.e. stable conditions of gas and sorbent phase. Particular focus during operation was set on achieving representative operation. To assure steady-state operation, the mean residence time of the sorbent was taken into account to estimate the required period to reach steady-state conditions in the solid phase. Three times the residence time of the sorbent in the system was utilized to ensure that at least 95% of the inventory is exchanged by the make-up flow. A particular focus of the evaluation was set on the carbonator reactor performance applying the methodology experienced from small scale facilities [24–26]. In these tests, different fuel types (see Table 1), hard coal and lignite, in different particle size distributions, pulverized or coarse (d_{50} see Table 1), were fuelled in the calciner. The main variables to be determined affecting the performance of the carbonator reactor are as follows (see Fig. 3):

Table 1
Composition of fuels (as received).

Component	Hard coal	Lignite	Unit
Fixed carbon	48.52	40.60	wt.%
Volatiles	25.70	45.70	wt.%
Moisture	11.50	9.90	wt.%
Ash	14.28	3.80	wt.%
Carbon	63.60	59.90	wt.%
Hydrogen	3.66	4.76	wt.%
Sulphur	0.64	0.32	wt.%
Nitrogen	1.55	0.69	wt.%
Oxygen	4.77	20.63	wt.%
Lower heating value (LHV)	24.32	22.92	MJ/kg
Median particle diameter (d_{50})	45/1500	36	µm

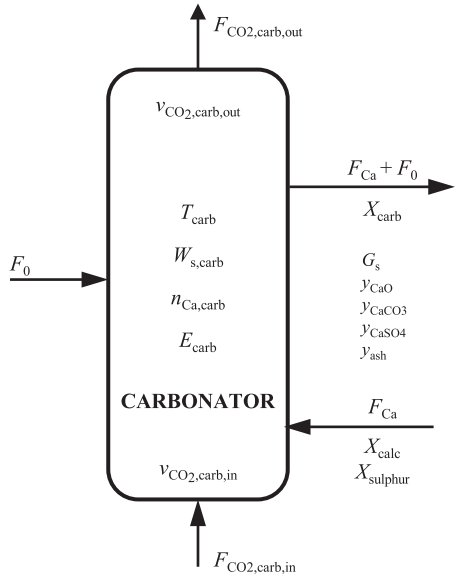


Fig. 3. Main flows and operating parameters of 1 MW_{th} carbonator reactor.

- The specific inventory of solids in the carbonator $W_{s,carb}$ is continuously determined by the measurement of the reactor pressure drop between the plane above the distributor and the exit of the reactor. Based on the chemical composition of the inventory, the Ca-based inventory can be determined ($n_{Ca,carb}$ in Fig. 3).
- The carbonator reactor temperature is averaged by the measurements along the reactor height since the bayonet cooling tubes imply a certain axial temperature profile. The entering solids from the calciner (850–940 °C) and the exothermic carbonation reaction heat up the bottom zone. As a consequence, the temperature needs to be controlled. Therefore, heat is extracted by the bayonet tubes and the colder solid stream internally recirculating control the bottom zone temperature. Consequently, the carbonator temperature is adapted to 630–700 °C (T_{carb} in Fig. 3).
- The flow of flue gas and its composition entering and leaving the carbonator is continuously measured, CO, CO_2, NO and SO_2 by nondispersive infrared spectroscopy, O_2 by a paramagnetic and H_2O by a psychometric measuring principle. The molar flows of CO_2 ($F_{CO2,carb,in}$,$F_{CO2,carb,out}$ in Fig. 3) can be calculated by the volumetric flow rates and the measured CO_2 concentrations.
- To close the carbon balance as well as the heat balance, it is crucial to determine the total circulating solid mass flow G_s and the molar circulation of Ca-based particles (F_{Ca} in Fig. 3), respectively, between carbonator and calciner reactor. With the help of the sorbent composition, the characteristic volumetric curve of the screw conveyor allows the calculation of the total solid circulating mass flow and the corresponding molar circulation rate.
- Frequent analyses of the composition solids transferred from carbonator to calciner and vice versa is required. The chemical composition in terms of CaO, $CaCO_3$, $CaSO_4$ and ash content is analyzed (y_{CaO},y_{CaCO3},y_{CaSO4},y_{ash} in Fig. 3), and the molar carbonate content of particles entering (X_{calc} in Fig. 3) and leaving (X_{carb} in Fig. 3) the carbonator can be determined. The extracted samples are tested with TGA and in the batch reactor to investigate CO_2 carrying capacity and reaction rates.

The CaL process was investigated in more than 2400 h of long-term pilot operation, thereof more than 1,200 h with continuous CaL operation capturing CO_2. 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. The main range of operating parameters during the long-term pilot tests is summarized in Table 2.

2.2. Evaluation

The trends observed during operation, especially in stead-state periods, are evaluated in terms of the efficiency of the process. The CO_2 absorption efficiency in the carbonator E_{carb} is a crucial parameter for process evaluation in terms of reactor design and scale-up purposes. It is defined as the flow of CO_2 absorbed related to the flow of CO_2 fed in the carbonator (see Fig. 3). The carbonator efficiency can be calculated as follows:

$$E_{carb} = \frac{F_{CO2,carb,in} - F_{CO2,carb,out}}{F_{CO2,carb,in}} \quad (2)$$

The maximum carbonator efficiency for removing CO_2 from the gas flow entering the carbonator ($E_{carb,eq}$) is limited by the minimum CO_2 volumetric concentration derived from the chemical equilibrium. It helps to compare the actual carbonator efficiency with the maximum possible efficiency at the current temperature. The chemical equilibrium is a function of the reactor temperature and is given in Eq. (3) from Silcox et al. [28]:

$$v_{CO2,eq} = 4.137 \times 10^7 e^{\frac{-20,474}{T}} \quad (3)$$

Besides the limitation of the absorption by the reactor temperature, the efficiency is dependent on the ratio of incoming flow of moles Ca from the calciner and the molar flow of CO_2 contained in flue gas entering the carbonator. To quantify this relation, the sorbent looping ratio *LR* is defined in Eq. (4):

$$LR = \frac{F_{Ca}}{F_{CO2,carb,in}} \quad (4)$$

The ability of the sorbent entering the carbonator to absorb CO_2 depends on the reactivity. The fresh limestone fed as make-up (F_0) mixes with the circulating stream to maintain and achieve a high quantity and quality of CaO. The make-up is quantified by the ratio of limestone fed to the process related to the CO_2 to be captured in the carbonator. Eq. (5) shows the make-up ratio *MR*.

$$MR = \frac{F_0}{F_{CO2,carb,in}} \quad (5)$$

The sorbent looping and the make-up ratios are of practical interest as operating parameters in the CaL process. The sorbent looping ratio influences the heat required for sorbent regeneration in the calciner. A low sorbent looping ratio is desired to limit the additional heat input to the calciner. The make-up ratio needs to be kept at low values to avoid additional heat input for calcination on the one hand, and on the other hand a certain amount is required to maintain a high reactivity of the sorbent. An optimum of both ratios has to be achieved in long-term operation.

Table 2
Range of operating parameters during long-term pilot tests.

Parameter	Variable	Value	Unit
Carbonator average temperature	T_{carb}	620–695	°C
Carbonator solids inventory	$W_{s,carb}$	325–815	kg/m^2
Carbonator inlet CO_2 volumetric fraction	$v_{CO2,carb,in}$	11–16	vol.%
Carbonator absorption efficiency	E_{carb}	45–95	%
Solid circulation flow between the reactors	G_s	2.5–4.2	kg/m^{2}s
Looping ratio	*LR*	9–20	mol_{Ca} /mol_{CO2}
Make-up ratio	*MR*	0.04–0.25	mol_{Ca}/mol_{CO2}
Calciner average temperature	T_{calc}	840–910	°C
Calciner inlet CO_2 volumetric fraction	$v_{CO2,calc,in}$	0–32	vol.%
Calciner inlet O_2 volumetric fraction	$v_{O2,calc,in}$	43–60	vol.%
Calciner inlet H_2O volumetric fraction	$v_{H2O,calc,in}$	0–12	vol.%

3. Results and discussion

3.1. Exemplary results of long-term operation

As described above this paper focuses on steady-state long-term operation. It may be of interest to discuss the approach to achieve steady-state operating periods. In general, an experimental test run starts with heating of the dual fluidized bed system following the temperature gradients of the refractory lining. In the beginning, both reactors are fluidized with electrically pre-heated air followed by the start-up burners. Sorbent is filled into the reactor system, and pressure sealing is achieved in the loop seals. Afterwards solid circulation is started and the mass flow from the carbonator to the calciner is stepwise increased. Stable hydrodynamics in the dual CFB system with a minimum of circulating are established. The circulating material heats up all interconnecting parts of the system. The reactors are continuously heated up, and at 700 °C in the calciner, coal firing is started to substitute the burner and is increased stepwise. The calcination of the sorbent takes place as the calciner is heated up to operating temperature. The solid circulation is further increased and utilized as a heat carrier to the carbonator to stop the start-up burner. The carbonator fluidization air is then enriched with CO_2 to start the CaL process. The starting carbonation reaction increases the reactor temperature that is controlled by the bayonet cooling tubes. The solid circulation is increased gradually to achieve stable CO_2 absorption in the carbonator. After establishing stable operation of the total system, the calciner operation is switched from air to oxy-combustion mode by replacing air with oxygen enriched flue gas. The carbonator fluidization is switched from artificial to coal originated flue gas from the combustion chamber. A continuous feed of make-up is started to adjust the sorbent activity as

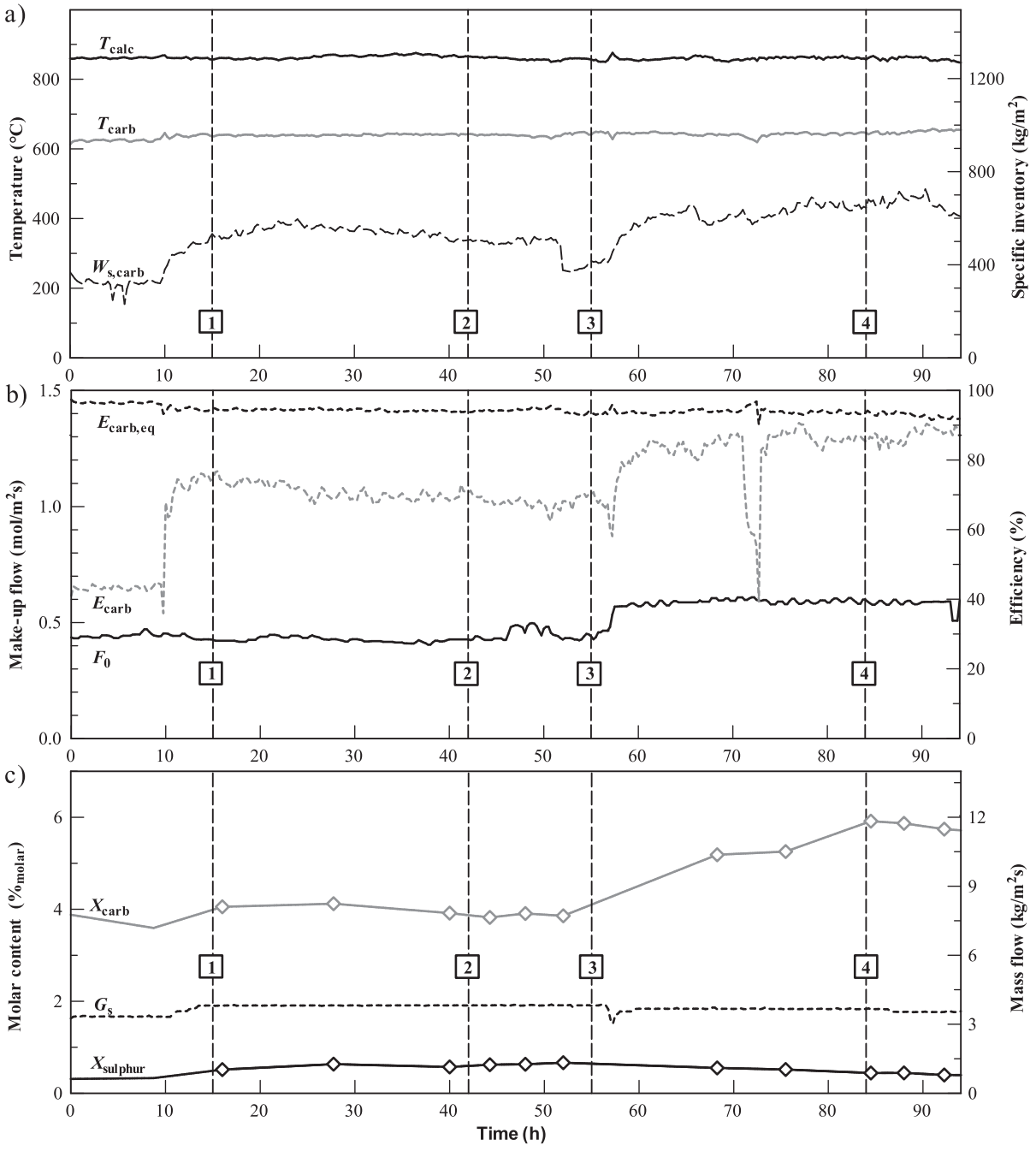


Fig. 4. Exemplary long-term pilot operation (transient to and between steady-states).

well as to replace the loss of fines due to attrition. Material is extracted from the reactors to keep the inventory constant while feeding make-up.

This general approach is used to achieve stable operation in the pilot plant during the test campaigns. Based on stable operation, single operating parameters such as make-up feed, solid circulation rate or reactor temperatures were varied to move on to another steady-state operating point.

Exemplary results from a CaL long-term test campaign using high grade pulverized lignite from the Rhenish area (see Table 1) as fuel and limestone (d_{50} = 175 µm, purity of 98.2 wt.% $CaCO_3$) from Western Germany are shown in Fig. 4.

The initial period until 15 h (1) shows the start of the CaL testing. The average temperatures in the carbonator and the calciner were adjusted to 650 °C and 870 °C, respectively, and were maintained during the entire test run (see Fig. 4a). At 10 h, the carbonator fluidization was switched from synthetic to coal originated flue gas from the combustion chamber with a superficial gas velocity of 2.3–2.5 m/s. The specific reactor inventory was increased from 300 kg/m^2 to around 600 kg/m^2 and was kept constant for the whole testing period (see Fig. 4a). Oxy-fuel combustion in the calciner was established using oxygen diluted with recirculated flue gas as fluidization media. The calciner was operated with a constant superficial gas velocity of 4.5–5.5 m/s and a lean zone temperature of around 900 °C to guarantee a full regeneration of the sorbent. The inventory was continuously replaced by a make-up feed of 0.4 mol/m^{2}s (see Fig. 4b) to guarantee a continuous mixing of inventory and fresh material, corresponding to a molar make-up ratio *MR* of 0.12 mol $CaCO_3$ per mol CO_2 fed to the carbonator. The solid flow circulating between the reactors was kept constant at 3.8 kg/m^{2}s (see Fig. 4c) corresponding to a sorbent looping ratio *LR* of 17 mol of Ca circulated per mol CO_2 fed to the carbonator reactor for the absorption process. In this initial phase, the absorption efficiency in the carbonator of around 55% was poor compared to the equilibrium CO_2 absorption efficiency calculated by the average carbonator temperature (see Fig. 4b). The established operating conditions were maintained for 40 h to achieve a homogeneous mixing of inventory and make-up in order to guarantee steady-state sorbent behaviour.

A transition phase from 15 h (1) to 42 h (2) is obvious wherein none of the operating parameters was changed. The carbonator absorption efficiency E_{carb} decreased from an initial value of 75% to a residual value of 70% (see Fig. 4b). The decrease of E_{carb} corresponded to the reduction of the flow of CO_2 absorbed in the carbonator ($F_{CO2,carb,in}E_{carb}$) from an initial value of 2.9 to 2.5 mol/m^{2}s.

The transition is reflected by the carbonate content of the loaded sorbent, X_{carb}, and the sulphur content $X_{sulphur}$. X_{carb} decreased from 4.1 to 3.8%$_{molar}$, reflecting a continuous deactivation of the sorbent and consequently the decrease of the reactivity. In the same time, $X_{sulphur}$ increased from 0.5 to 0.7%$_{molar}$ reflecting the accumulation of inactive material (see Fig. 4c).

After 42 h (2) steady-state operation was achieved. In this phase, steady-state conditions were recognizable by the constant CO_2 absorption in the gas phase (see Fig. 4b). The solid analyses of three samples in this period proved the steadiness in the sorbent phase by a constant carbonate content of 0.038 mol$_{CaCO3}$/mol$_{Ca}$ and sulphur of 0.007 mol$_S$/mol$_{Ca}$, as shown in Fig. 4c.

At 55 h (3), the make-up feed to the process was increased from 0.4 to 0.6 mol/m^{2}s (*MR* of 0.17) to adjust the sorbent performance whilst the other operating parameters were kept constant. Fig. 4b shows the effect on carbonator absorption efficiency. It increased significantly from 70 to 90% in a period of 30 h, representing conditions close to the thermodynamic equilibrium The corresponding flow of absorbed CO_2 increased from 2.5 to 3.1 mol/m^{2}s. At the same time, X_{carb} increased from 3.8 to 5.7%$_{molar}$, and $X_{sulphur}$ decreased from 0.7 to 0.4%$_{molar}$. It reflects the higher loading of the circulating sorbent due to a higher activity since more fresh material is added to the process and more inactive material is replaced. This operation period was shortly interrupted at 72 h when a combustion chamber shut-down forced carbonator fluidization by artificial flue gas for 30 min. During this period, less CO_2 and the absence of H_2O in the carbonator fluidization led to a decrease of T_{carb} to 615 °C, and as a consequence E_{carb} dropped.

The transition phase ended after 30 h and at 85 h (4) and a second steady-state operating period was reached representing stable conditions in gas as well as sorbent phase.

The results from the pilot tests show carbonate contents X_{carb} of 0.03–0.1 mol$_{CaCO3}$/mol$_{Ca}$ at the carbonator outlet indicating the residual activity of the sorbent. The low carbonate contents indicate a high sorbent deactivation at the tested conditions. Especially at a low make-up ratios (*MR* < 0.15), the sorbent deactivation is high indicating the lower end in this range. Make-up rations higher than 0.15 are required to significantly increase the activity of the material to achieve molar carbonate contents X_{carb} of 0.1 mol$_{CaCO3}$/mol$_{Ca}$, and thus ensuring carbonator absorption efficiencies higher than 90%.

Steady-state operating points with different fuel type and preparation (see Table 1) were used to point out the influence on sorbent composition. The comparison of sorbent compositions between pulverized hard coal and lignite tests shows differences in the share of $CaSO_4$ and ash. The low sulphur content of lignite is reflected by $CaSO_4$ fractions in a range 0.25–1.6 wt.%, compared to 2–12 wt.% for hard coal. The lower ash content of the lignite fuel is represented by ash fractions of 3–6 wt.% against 6–16 wt.% for the hard coal case as well. Comparing the ash and $CaSO_4$ fractions of sample analyses from hard coal testing with different fuel preparations, no significant difference in the share of $CaSO_4$ can be observed whereas the accumulation of ash is higher fuelling the hard coal in coarse form. Up to 20 wt.% of ash accumulates in the sorbent stream and the conclusion can be drawn that the particle size of the coal significantly affects the share of ash since the separation efficiency of ash particles in the calciner cyclone is influenced. The bigger the ash particles, the more ash is separated and accumulates in the circulating material.

The energy consumption for CaL CO_2 capture derived from the pilot tests was between 6 and 10 MJ/kg$_{CO2}$. The related penalties in terms of net efficiency caused by ASU and make-up were in a range of 1.9–2.9%-points and 0.8–3.1%-points, respectively. It is noteworthy to mention that the heat losses in the 1 MW$_{th}$ are significantly higher compared to larger size reactor systems and thus will decrease with increasing scale.

3.2. Closure of CO_2 balance

An important factor of process evaluation is the closure of the CO_2 mass balance with a certain focus on the carbonator. During steady-state operation, the CO_2 removed from the gas phase as well as inserted CO_2 with the make-up can be calculated and compared with the $CaCO_3$ formed in the circulating stream of CaO. Hence, the following mass balance has to be fulfilled:

$$F_{CO2,carb,in}E_{carb} = F_{Ca}(X_{carb} - X_{calc}) \quad (6)$$

The CO_2 removed from the gas phase can be calculated by the flow and gas composition measurement at the inlet and outlet of the carbonator. Thus, the terms on the left side of Eq. (6) are most reliable. The solid phase on the right side of Eq. (6) included the molar flow F_{Ca} representing the amount of CaO particles that enter the carbonator with a molar carbonate content X_{calc} after regeneration and leave the reactor after absorption with the carbonate content X_{carb}. F_{Ca} is calculated from the total circulating solid mass flow G_s and the solid samples taken from the reactor system. The total solid circulation rate G_s during steady-state conditions is derived from the volumetric characteristic curve of the screw conveyor transporting the material between the reactors and the mass fractions of the material ($y_{CaO}, y_{CaCO3}, y_{CaSO4}, y_{ash}$). The molar flow F_{Ca} can be calculated by Eq. (7), taking into account the mass fraction of Ca particles (y_{Ca}) and the average molar weight of these solids (M_{Ca}):

$$F_{Ca} = \frac{G_s y_{Ca}}{M_{Ca}} \quad (7)$$

The fraction of impurities, either representing deactivated calcium sulphate (y_{CaSO4}) or inactive ash (y_{ash}), is strongly dependent on the type and particle size of fuel burnt in the calciner. During the test, the solid analyses show significantly lower fractions of calcium sulphate and ash fuelling the pulverized Rhenish lignite compared to the hard coal. The lignite contains significantly lower fractions of sulphur and ash (see Table 1) that is reflected by solid analyses. The influence of fuel properties on the sorbent requires a more deeper evaluation.

The CO_2 balance of Eq. (6) can be closed with the help of Eq. (7). The two terms of Eq. (6) are compared in Fig. 5. The CO_2 removed from the gas phase in the carbonator and the increase of $CaCO_3$ in solid circulating flow between the reactors is depicted. The comparison includes the results from various operating points, operated under a broad range of parameters, e.g reactor inventory and temperature, make-up feed, solid circulation etc. For all operating points, solid samples from the reactors were extracted and considered for each point in the balance. As it can be seen from Fig. 5, the CO_2 bound in the solid phase matches the CO_2 removed from the gas phase with a reasonable deviation.

3.3. Active space time

The application of a basic reactor model to the experimental data is particularly useful to evaluate the results and for designing the carbonator. Eq. (8) shows the balance of CO_2 absorbed in the gas phase (left term) and the amount of solids in the carbonator reacting with the CO_2 with an average reaction rate (right term).

$$F_{CO2,carb,in} E_{carb} = n_{Ca,carb,active} (dX/dt)_{carb} \quad (8)$$

The reaction rate of the particles in the carbonator is based on the assumption that the present particles react with a constant rate until a maximum conversion rate (X_{ave}). A perfectly mixed reactor for the solid phase and a plug flow reactor for the gas phase is assumed. This model has been applied for various tests to evaluate experimental results [16,26]. According to the methodology postulated by Charitos et al. [26], the reaction rate depends on the sorbent constant k_s, the gas–solid contacting factor φ, the CO_2 carrying capacity X_{ave} and the difference between the average and equilibrium CO_2 volume fraction in the reactor. The reaction rate is shown in Eq. (9).

$$(dX/dt)_{carb} = \varphi k_s X_{ave} (\overline{\nu_{CO2,carb}} - \nu_{CO2,carb,eq}) \quad (9)$$

The active inventory $n_{Ca,carb,active}$ can now be defined based on the reaction rate term. According to the postulated model, only an active fraction (f_{active}) of the particles $n_{Ca,carb}$ taking part in the kinetically controlled fast reaction regime. The active fraction corresponds to particles with a residence time below the time needed to increase the carbonate content from X_{calc} to X_{ave} (t^*). The active fraction is calculated with the results of solid sample analyses inserted in the reaction rate model in Eq. (9).

$$f_{active} = 1 - e^{\left(\frac{-t^*}{n_{Ca,carb}/F_{Ca}}\right)} \quad (10)$$

The combination of Eq. (8) with Eqs. (9)–(12) leads to an expression describing the carbonator efficiency of a CaL system by including all directly or indirectly linked operating parameters, the so-called active space time (τ_{active}).

$$E_{carb} = \tau_{active} \varphi k_s (\overline{\nu_{CO2,carb}} - \nu_{CO2,carb,eq}) \quad (11)$$

For given operating conditions, the active space time in Eq. (11) indicates the performance of the carbonator as a single parameter. The inventory, the residence time of particles, the CO_2 concentrations and temperature as well as limestone dependent influences are considered.

$$\tau_{active} = \frac{n_{Ca,carb}}{F_{CO2,carb,in}} f_{active} X_{ave} \quad (12)$$

The apparent carbonation rate constant within the carbonator reactor ($k_s\varphi$) can be derived as a fitting factor from Eq. (11). The carbonation rate constant k_s can be measured from TGA experiments. An averaged value of 0.16 s^{-1} was obtained.

A simplification has been made to apply the active space time model to the experimental data. As already reported by Charitos et al. [26], the values of X_{ave} and X_{carb} are very close for residence times around 3 min in the carbonator. In pilot operation, the carbonator was operated with a residence time of particles in this range and consequently, the simplification was made to use X_{carb} instead of X_{ave} for the evaluation of this set of experimental data.

The comparison of CO_2 removed from the gas phase and the CO_2 reaction in the carbonator bed applying the active space time is shown in Fig. 6. A reasonable agreement of the model with the experimental data is accomplished taking under consideration that there are inherent uncertainties in the determination of the parameters applied in this model, as discussed by Rodriguez et al. [25,29]. The estimation of solid circulation rate is challenging since it is a difficult parameter to be measured in a CFB system. The determination of average carbonate conversion is sensible for experimental uncertainties as well since the extracted solid samples are only a very little share compared to the inventories and streams in the pilot plant. Nevertheless the results from CO_2 balances closures as depicted in Figs. 5 and 6 are according to results from other pilots. The evaluation provides confidence about the scalability in terms of carbonator absorption efficiency.

4. Conclusions

An important step towards the realization of the CaL technology in commercial scale is the successful pilot testing in 1 MW_{th} scale. Semi-industrial pilot testing of the CaL process with more than 1,200 h of stable CO_2 capture showed the maturity of the process realizing CO_2 absorption rates in the carbonator higher than 90% and overall CO_2 capture rates higher than 95%. The experimental results prove the performance of the process under a wide range of parameters in steady-state operation.

The procedure to achieve steady-state operation has been demonstrated under oxy-fuel calcination using vari-ous fuel types and preparations. Up to 60 h are required to provide a homogenous mixing of the existing inventory with fresh make-up sorbent with respect to a

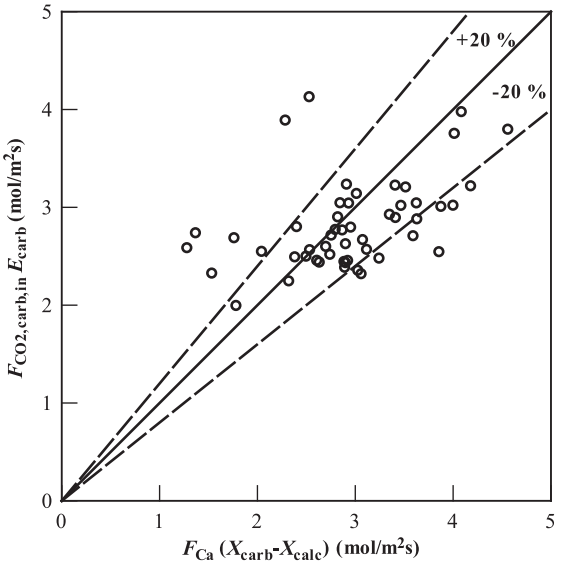


Fig. 5. Closure of carbon molar balance between removed CO_2 from the gas phase and increment in circulating solid stream between reactors.

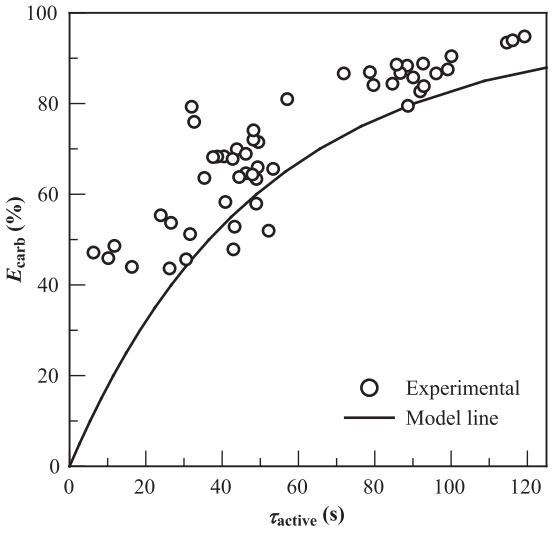


Fig. 6. Carbonator efficiency vs. active space time for experimental steady-states.

steady sorbent performance and accumulation of impurities. The impact of the make-up ratio on the carbonator absorption efficiency and the accumulation of sulphur in the sorbent are exemplarily shown. Make-up ratios of more than 0.15 are feasible to keep the activity of the sorbent sufficient and the share of inactive material low to achieve carbonator absorption rates higher than 90%. The accumulation of inert material shows the dependency on ash and sulphur fractions of the fuel in the calciner. High grade fuel reduce the inactive sorbent share in comparable operation conditions from around 20 to 8 wt.%.

The satisfying closure of carbon balance and the interpretation of the results with the help of a basic reactor model provide the confidence for a scale-up of the technology to a demonstration plant in 20 MW_{th} scale. An active space time of 80 s is identified as the basis for 90% of absorption efficiency in the carbonator. This comprehensive data base of experimental results under realistic operating conditions is applied for the further development of the CaL technology.

Acknowledgements

The research leading to these results has received funding from the European Union's Seventh Framework Programme (FP7/2007–2013) under grant agreement No. 608578 (SCARLET-www.project-scarlet.eu) and from the German Federal Ministry of Economic Affairs and Energy based on a resolution of the German Parliament (LISA2 - FKZ: 03ET7018). The financial contribution of GE, RWE, Uniper, Steinmüller Babcock Engineering and Rheinkalk is gratefully acknowledged. We thank Lhoist Recherche et Développement S.A. for the extensive analyses of solid samples.

References

[1] Shimizu T, Hirama T, Hosoda H, Kitano K, Inagaki M, Tejima K. A twin fluid-bed reactor for removal of CO_2 from combustion processes. Chem Eng Res Des 1999;77:62–8.
[2] Abanades JC, Anthony EJ, Wang JS, Oakey JE. Fluidized bed combustion systems integrating CO_2 capture with CaO. Environ Sci Technol 2005;39:2861–6.
[3] Martínez I, Murillo R, Grasa G, Rodríguez N, Abanades JC. Conceptual design of a three fluidised beds combustion system capturing CO_2 with CaO. Int J Greenhouse Gas Control 2011;5:498–504.
[4] Junk M, Reitz M, Ströhle J, Epple B. Thermodynamic evaluation and cold flow model testing of an indirectly heated carbonate looping process. Chem Eng Technol 2013;36:1479–87.
[5] Reitz M, Junk M, Ströhle J, Epple B. Design and operation of a 300 kW_{th} indirectly heated carbonate looping pilot plant. Int J Greenhouse Gas Control 2016;54(Part 1):272–81.
[6] Hanak DP, Kolios AJ, Manovic V. Comparison of probabilistic performance of calcium looping and chemical solvent scrubbing retrofits for CO_2 capture from coal-fired power plant. Appl Energy 2016;172:323–36.
[7] Hanak DP, Manovic V. Calcium looping with supercritical CO_2 cycle for decarbonisation of coal-fired power plant. Energy 2016;102:343–53.
[8] Zhu L, Jiang P, Fan JM. Comparison of carbon capture IGCC with chemical-looping combustion and with calcium-looping process driven by coal for power generation. Chem Eng Res Des 2015;104:110–24.
[9] Abu Zahra MRM, Fernandez ES, Goetheer ELV. Guidelines for process development and future cost reduction of CO_2 post-combustion capture. Energy Procedia 2011;4:1051–7.
[10] Zhao M, Minett AI, Harris AT. A review of techno-economic models for the retrofitting of conventional pulverised-coal power plants for post-combustion capture (PCC) of CO_2. Energy Environ Sci 2013;6:25–40.
[11] Cormos CC. Economic evaluations of coal-based combustion and gasification power plants with post-combustion CO_2 capture using calcium looping cycle. Energy 2014;78:665–73.
[12] European Commission, HORIZON 2020 Work Programme 2016–2017 Annex G. Technology readiness levels (TRL), 2017. URL http://ec.europa.eu/research/participants/data/ref/h2020/other/wp/2016-2017/annexes/h2020-wp1617-annex-gaen.pdf.
[13] Abanades JC, Arias B, Lyngfelt A, Mattisson T, Wiley DE, Li H, et al. Emerging CO_2 capture systems. Int J Greenhouse Gas Control 2015;40:126–66.
[14] Dieter H, Bidwe AR, Varela-Duelli G, Charitos A, Hawthorne C, Scheffknecht G. Development of the calcium looping CO_2 capture technology from lab to pilot scale at IFK. University of Stuttgart, Fuel 2014;127:23–37.
[15] Ströhle J, Junk M, Kremer J, Galloy A, Epple B. Carbonate looping experiments in a 1 MW_{th} pilot plant and model validation. Fuel 2014;127:13–22.
[16] Arias B, Diego ME, Abanades JC, Lorenzo M, Diaz L, Martinez D, et al. Demonstration of steady state CO_2 capture in a 1.7 MW_{th} calcium looping pilot. Int J Greenhouse Gas Control 2013;18:237–45.
[17] Chang M-H, Chen W-C, Huang C-M, Liu W-H, Chou Y-C, Chang W-C, et al. Design and experimental testing of a 1.9MW_{th} calcium looping pilot plant. Energy Procedia 2014;63:2100–8.
[18] Barker R. The reversibility of the reaction $CaCO_3 \Leftrightarrow CaO + CO_2$. J Appl Chem Biotechnol 1973;23:733–42.
[19] Abanades JC. The maximum capture efficiency of CO_2 using a carbonation/calcination cycle of $CaO/CaCO_3$. Chem Eng J 2002;90:303–6.
[20] Khinast J, Krammer GF, Brunner C, Staudinger G. Decomposition of limestone: the influence of CO_2 and particle size on the reaction rate. Chem Eng Sci 1996;51:623–34.
[21] García-Labiano F, Abad A, de Diego LF, Gayán P, Adánez J. Calcination of calcium-based sorbents at pressure in a broad range of CO_2 concentrations. Chem Eng Sci 2002;57:2381–93.
[22] Martínez I, Grasa G, Murillo R, Arias B, Abanades JC. Kinetics of calcination of partially carbonated particles in a Ca-looping system for CO_2Capture. Energy Fuels 2012;26:1432–40.
[23] Helbig M, Hilz J, Haaf M, Daikeler A, Ströhle J, Epple B. Long-term carbonate looping testing in a 1 MW_{th} pilot plant with hard coal and lignite. Energy Procedia 2017;114:179–90.
[24] Alonso M, Rodríguez N, Gonzalez B, Grasa G, Murillo R, Abanades JC. Carbon dioxide capture from combustion flue gases with a calcium oxide chemical loop. Experimental results and process development. Int J Greenhouse Gas Control 2010;4:167–73.
[25] Rodríguez N, Alonso M, Abanades JC. Experimental investigation of a circulating fluidized-bed reactor to capture CO_2 with CaO. Aiche J 2011;57:1356–66.
[26] Charitos A, Rodríguez N, Hawthorne C, Alonso M, Zieba M, Arias B, et al. Experimental validation of the calcium looping CO_2 capture process with two circulating fluidized bed carbonator reactors. Ind Eng Chem Res 2011;50:9685–95.
[27] Kremer J, Galloy A, Ströhle J, Epple B. Continuous CO_2 capture in a 1-MW_{th} carbonate looping pilot plant. Chem Eng Technol 2013;36:1518–24.
[28] Silcox GD, Kramlich JC, Pershing DW. A mathematical model for the flash calcination of dispersed $CaCO_3$ and $Ca(OH)_2$ particles. Ind Eng Chem Res 1989;28:155–60.
[29] Rodríguez N, Alonso M, Abanades JC, Charitos A, Hawthorne C, Scheffknecht G, et al. Comparison of experimental results from three dual fluidized bed test facilities capturing CO_2 with CaO. Energy Procedia 2011;4:393–401.