Effect of CO₂ on high temperature chlorination behavior of calcined limestone in an innovated fixed-bed reactor

Geng-Min Lin, Chien-Song Chyang^{*}

Department of Chemical Engineering, Chung Yuan Christian University, Chung Li 32023, Taiwan, R.O.C.

Corresponding author. Tel.: +886 3 2654119; fax: +886 3 4636242.

E-mail address: cschyang@cycu.edu.tw (C.S. Chyang).

Abstract: This work aimed to elaborate on the influence of CO₂ on the reactivity of CaO with HCl under conditions similar to combustion environment. This study was conducted in an innovated fixed-bed reactor to investigate the influences of simulated CO₂ concentrations on the chemistry of CaO with HCl at varied temperatures. Tests of sole CaO carbonation and chlorination were performed in a thermogravimetric analyzer and fixed-bed reactor, respectively, to provide fundamental information for the CaO chlorination experiments in the presence of CO₂. The HCl concentrations were continuously monitored in a Fourier Transform Infrared (FTIR) cell and the repeatability tests yielded good results. These results indicated that the presence of CO₂ was beneficial for the apparent reaction rates of CaO chlorination performed at 650 °C and 700 °C, compared with the case of only chlorination; nevertheless, this benefit accompanied a slight reduction of HCl capture capacity. The results were related to the CaO carbonation behavior. On the

other hand, further increased CO₂ concentrations had no effect on the extent of the chlorination reaction.

Keywords: CaO; chlorination; carbonation; breakthrough curve; FTIR

1. Introduction

The generation of hydrogen chloride (HCl) during the incineration processes of chlorine-containing waste is an inevitable consequence. Removal of HCl from the flue gas is necessary and important due to its polluting, harmful and corrosive nature. The oxidation of HCl to Cl₂ under a particular condition, known as the Deacon reaction, may become precursors of dioxin compounds [1-10]. That is, the presence of HCl may lead to the formation of PCDD/Fs in the low-temperature regime. Current acid gas removal processes in industry customarily employ scrubbers (such as wet, semi-dry and dry mechanisms) to reduce gas emissions before the flue gases are discharged. However, those scrubbing processes operate at a temperature that is lower than that of PCDD/Fs formation, especially for the wet scrubbing processes. This means that the scrubbing processes may increase the risk of dioxin compound formation. Thus, the removal of HCl to acceptable levels before the flue gases are cooled is a promising method for hazardous emission reduction. Adding sorbents (such as limestone) to the bed zone of the incinerator can preliminarily reduce the HCl in the flue gas [11], decrease the possibility of corrosion and dioxin formation in the incinerator [7, 12-14] and lower the scrubber loading. The injection of limestone into fluidized bed

combustors (FBCs) is a suitable solution in removing acidic gases at high temperatures because of the advantage of continuous operation in the fluidized bed combustor.

Over the past two decades, much attention has focused on the influence of the physical properties of sorbents, acid gas concentrations, the reaction temperatures on the HCl capture efficiency and the kinetics and thermodynamics of HCl with sorbents. Among those studies, many are concerned with the HCl capture by slaked lime at temperatures lower than that employed in FBC. This concern originates with wet scrubber technology that has been widely used throughout industry. Some previous studies [2, 15-17] researching the chlorination of lime or limestone at elevated temperature have led to the conclusion that the maximum HCl capture capacity occurs approximately 650 °C and decreases rapidly as the temperature continues to rise. Chyang *et al.* [17] suggested that the decrease of HCl capture capacity can be ascribed to the change of reaction equilibrium. For lower temperatures, various investigations [18-22] have revealed that the HCl capture capacity of CaO increases with temperature in the range of 150 to 600 °C.

However, the gas atmosphere must be taken into consideration in regard to the practical applications of adding sorbents into the combustor to immediately remove HCl. The removal of HCl using Ca-based sorbents has been widely investigated; however, the influence of other gas species in the flue gas on the reactivity of sorbent with HCl has not been extensively explored, especially at high temperatures. For the HCl capture by limestone in the FBC, the calcination and

recarbonation reactions of sorbents may also be included because conditions of high temperature and the presence of CO₂ are unavoidable. Therefore, the following reactions are of important:

If the temperature is high enough (above 700 °C) and the partial pressure of CO₂ is below the equilibrium pressure, the calcination process in (1) will proceed. On the contrary, the reverse reaction in (1), referred to as the recarbonation process, may be favored as the temperature decreases or the CO₂ partial pressure is high enough.

Because of the lack of information on the HCl capture by CaO under conditions similar to fluidized bed combustors (temperature, gaseous species and its concentrations), the objective of this work was to elaborate on the influence of CO₂ on the reactivity of CaO with HCl in the presence of 0-12% CO₂ at high temperatures (650-850 °C). The behavior of CaO carbonation were also tested under the same operating conditions (CO₂ partial pressures and temperatures).

2. Material and methods

The tests were conducted in both a thermogravimetric analyzer (TGA) and an innovated fixed-bed reactor system. The CaO carbonation tests were performed in a Perkin-Elmer TGA; the CaO chlorination in the presence and absence of CO₂ were also examined in the fixed-bed reactor

system. Prior to the CaO carbonation tests, the CaCO_3 was calcined at $800\text{ }^{\circ}\text{C}$ in N_2 for 30 minutes. This calcination was used to ensure the CaCO_3 was fully converted to CaO before the temperature and reacting gases were brought to the desired conditions for carbonation.

2.1 Apparatus and Details

Based on previous experience, a fixed-bed reactor system was designed and developed. Some common problems with the fixed-bed reactor system that were improved upon for this study include the gas leakage of the reactor, especially at high temperatures, the cooling efficiency and space requirement. The entire fixed-bed reactor system (shown schematically in Fig. 1) was designed and developed to study high temperature gas-solid reactions. The system consisted of several sections, as follows: a bench-scale fixed-bed reactor with a height of 564 mm, a reacting gas supply system, an electric heating column, a purge gas system and a gas analyzer. The fixed-bed reactor was made of quartz to prevent corrosion and oxidation problems; the reactor occupied a small space and a facilitated a rapid cooling process (see Fig. 2). The entire reactor was comprised of three quartz units. The middle quartz unit was an air cooler with five tubes utilized to cool. A quartz-sintered plate was installed inside the inner tube (I.D. 13 mm) at 40 mm below the top of the tube to support the sorbent mixture. The reaction temperature was measured by a K-type thermocouple placed directly under the sample holder and controlled by a PID controller. Stainless-steel mass flow controllers (MFC) were used to precise and individual control the flow rate of all of the gas species,

including N_2 , CO_2 and HCl . Accordingly, the concentrations of the gas components (HCl and CO_2) were adjusted by the controllers. Once all of the gas species were mixed in the chamber, the mixture was introduced immediately into the reactor via a side inlet tube. The gas mixture first flowed upwards through an annulus region that is enclosed by two concentric tubes (I.D. 46 mm for the outer tube) for preheating. The mixture then flowed downwards through the inner tube and sample holder; finally, it was rapidly cooled in the cooler section. According to the trials, the temperature of exhaust gases ranged from 32 to 36 °C while the reactor was operated at 650-850 °C. Afterward, the exhaust gases were immediately introduced into the FTIR gas analyzer (MB 3000 series, Asea Brown Boveri) where the HCl concentration was continuously measured and registered. Finally, the exhaust gases were scrubbed in a dilute NaOH solution before discharge.

Prior to start each run, a simple and useful method was used to examine the gas leakage of the fixed-bed reactor; the reactor was reassembled in case of gas leakage. Teflon and silicon hoses were employed in this experimental system, depending on gas species and temperatures. In addition, to reduce the residence time required for exhaust gases to flow from the outlet tube to FTIR cell, the length of the Teflon hose was as short as possible. Such a method did not only reduce the residence time, but it also reduced the deviation while evaluating sorbent conversion degree. A three-way valve was used to redirect the HCl gas flow into a diluted NaOH solution before the experiments commenced. Immediately after the HCl gas flow was switched from the bypass to the gas-mixing chamber, the experiment began and the data were registered instantly. The system was purged with

dry air and N₂ before and after the experiments to ensure a clean system for the next run.

2.2 Material Preparation

The sorbent used in this study was commercial limestone (calcium carbonate, CaCO₃) and was screened to a particle size of 500-590 µm (35-30 mesh). Using a 1:10 ratio (limestone/sand), the sorbent was mixed with silica sand, which was screened to the same particle size as the limestone. The sorbent and silica sand were weighed on a high precision analytical balance (Sartorius, BAS124S-CW) for a total weight of 1.100 g (±0.001 g). After the sorbents and inner particles were well mixed, the mixture was loaded on the sample holder. The reactor was assembled immediately to examine the gas leakage prior to the experiment. The experimental procedure involved thermal decomposition of limestone and the chlorination reaction of CaO with HCl. The limestone in the mixture was first calcined at 800 °C for 30 min, and the N₂ flow rate was kept at 1000 sccm for sweeping out the CO₂ generated from the thermal decomposition. Then, the experiment subsequently began.

To choose the practical gas compositions such as those for HCl and CO₂, the gas atmosphere in the incineration process was taken into consideration. Three cylinders used in the experiments contained 900 ppm HCl in N₂, 99.9999% CO₂ and 99.99% N₂. The chlorination tests were operated at atmospheric pressure in the presence of ca. 461 ppm HCl and 0-12% CO₂ in dry N₂. The experiments were stopped when either the HCl outlet concentration was equal to the input value or

when the concentration of HCl remained relatively unchanged.

2.3 Analysis of Breakthrough Curves

Using the FTIR to continuously monitor the gaseous components discharged during reaction processes is a rapid and valid method, especially under conditions in which two or more reacting gases are involved in the gas-solid reaction. In this case, the CaO can simultaneously react with CO₂ and HCl and the conversion degree of CaO to form CaCl₂ can then be calculated individually by means of analyzing the time-dependent HCl concentration variations, which is also called the breakthrough curve (BC). This method is not affected by the simultaneous chlorination and carbonation reactions of CaO because the HCl outlet concentration profile can indirectly reflect the sorbent capacity of chlorination. The following section will develop and describe the expression of sorbent conversion degrees derived from the gas phase mass balance.

The total moles of gas component, *i*, entering the reactor during the reaction process, $N_{i,total}$ (*mol*), can be expressed as follows:

$$N_{i,total} = F_{i,0} \times t_{eq} \quad (4)$$

where $F_{i,0}$ is the inlet molar flow rate of gas component, *i* (*mol/min*); t_{eq} is the reaction time required for reaching the equilibrium state. The area under the breakthrough curve represents the unreacted moles of the gas component discharged from the reactor, $N_{i,lost}$ (*mol*). Therefore, the $N_{i,lost}$ can be obtained using the following equation:

$$N_{i,lost} = v_m \int_{t=0}^{t=t_{eq}} C_{i,e} dt = \frac{v_m}{24.465 \times 10^3} \int_{t=0}^{t=t_{eq}} C_{ppmv} dt \quad (5)$$

where v_m and $C_{i,e}$ stand for the volumetric flow rate of the gas mixtures (Nm^3/min) and the outlet concentration of the gas component, i , in the gas mixtures (mol/Nm^3), respectively. At any time, t (less than t_{eq}), the moles of the gas component reacted with the sorbent, N_{rx} (mol), can be written as:

$$N_{rx,t} = v_m \times (C_{i,0} \times t - \int_{t=0}^{t=t} C_{i,e} dt) \quad (6)$$

where $C_{i,0}$ is the inlet concentration of the gas component, i , in the gas mixtures. Considering a general gas-solid reaction and its stoichiometric coefficients, the conversion expression at any time is then obtained:

$$X_{A,t=t} = \frac{v_m \times (C_{i,0} \times t - \int_{t=0}^{t=t} C_{i,e} dt)}{b \times N_{A,0}} \quad (8)$$

where $N_{A,0}$ is the initial moles of A loaded in the reactor.

2.4 Experimental repeatability of the fixed-bed reactor system

Chlorination experiments under the same conditions were repeated three times to examine the reliability and repeatability of those data performed in the fixed-bed reactor system. The results indicate the repeatability of those curves is found to be good and that the difference among the curves is acceptable, as shown in Fig. 3. It also shows that the experimental data obtained by FTIR analyzer are reliable.

3. Results and discussion

3.1 Carbonation processes of CaO

The carbonation tests of calcined limestone used in the current study were carried out in the presence of 4-12% CO_2 at high temperatures (650-800 °C) to provide information for subsequent CaO chlorination experiments in the presence of CO_2 , and the results are presented in Fig 4. The tests under 100% CO_2 were also performed for reaction rate comparison. For the carbonation tests operated at atmospheric pressure, the CO_2 concentration employed corresponds to the ratio of the CO_2 partial pressure to the total gas pressure of gas mixtures.

As shown in Fig. 4a, the carbonation reaction of CaO does not occur even when the CO_2 concentration reached 12% at 800 °C. This suggests the reaction is not favored at studied CO_2 concentration as long as the operating temperature exceeds 800 °C. Additionally, similar behavior can also be observed in the presence of 4% CO_2 at 700 °C in Fig. 4c, which may be not surprising because the CO_2 partial pressure is lower than the decomposition pressure of CaCO_3 . A particular example can be observed in Fig. 4b. At this temperature, even though the CO_2 partial pressure is sufficient to achieve the carbonation, the reaction proceeds at a relatively slow rate due to the less favorable conditions. On the other hand, in the presence of 100% CO_2 at the studied temperatures, the carbonation reactions are all strongly favored and reaches a conversion close to 65% within 20 min due to the stronger driving force behind furthering the carbonation reaction. Fig. 4c and 4d also presents some cases of favorable carbonation process. In this cases, the carbonation processes of CaO transpires vigorously and reaches similar conversion degree. These results accounts for that the CO_2 partial pressure is far above the equilibrium pressure, which strongly depended on the

temperature. Accordingly, although the reaction temperature and CO_2 partial pressure are major parameters that control the direction and rate of the carbonation reaction, the extent of the reaction is hardly affected by those two factors even in case of relatively slow rate (as shown in Fig 4b) as long as the condition permits the carbonation to take place. The results of carbonation tests will be used as a reference or information for the subsequent simultaneous chlorination and carbonation experiments of CaO in the fixed-bed reactor system under the same operating conditions.

Although the lime precursor contains some impurities, the results of carbonation tests are still expected on the basis of the NIST-JANAF thermochemical tables [23, 24]. Another notable result is that, for the conditions that could lead to CaO carbonation, the reaction extent of each run reaches the same degree (approximately 65%) and does not obviously vary with temperature or CO_2 concentrations. This is perhaps not surprising, since the CaO sorbents derived from various limestone precursors have quite different utilization efficiencies [25-27]. Besides, the utilization efficiencies of calcium-based sorbent can also be improved by means of reactivation processes [28-30] or calcination conditions [27, 31].

3.2 Chlorination processes of CaO

In this research, the performances of chlorination reaction of calcined limestone in the innovated fixed-bed reactor are described through the concept of the breakthrough curve, *i.e.*, the analytic concentration profile as a function of time.

First, the chlorination tests of CaO were performed in the gas atmosphere of 461 ppm HCl in N₂ at 650-850 °C without the presence of CO₂ to provide a comparison with the experimental runs of simultaneous chlorination and carbonation of CaO. The breakthrough curves are plotted in Fig. 5. Additionally, the conversion curves of CaO to form CaCl₂ versus time are also shown in Fig. 5. It is clear that the CaO conversion reaches a maximum at 650 °C and starts to decrease with rising temperature. Again, additional effort is made to examine the HCl capture capacity of CaO at 600 °C, and the result reveals that the conversion degree is roughly 53%, lower than that at 650 °C and 700 °C. Interestingly, it is found that both of the final HCl concentrations of Fig. 5a do not reach the inlet value, implying that the chlorination processes are still proceeding at a very slow reaction rate. This can be attributed to the strong diffusion resistance of the CaCl₂ layer. On the other hand, as the reactions are operated above 750 °C, it takes less than 1/4 of the time required to reach equilibrium at 650 °C and 700 °C.

For all of the experiments in Fig. 5, these conversion curves demonstrate a typical example of gas-solid reactions of unchanging size. Some investigators [21, 32-35] mentioned that the gas-film and pore diffusion is unlikely to control the overall reaction rate. The HCl capture capacity of CaO increases linearly with time in the beginning of the reaction, indicating a chemical reaction controlling regime [36]. During the initial stage of gas-solid reaction with little or no product layer formation, the overall reaction rate is virtually controlled by the chemical reaction on the sorbent surface. Therefore, most of the conversion is achieved within 50 minutes in Fig. 5b and 100 minutes

in Fig. 5a. Later, the reaction rate starts to gradually slow due to the development of the product layer (CaCl_2), resulting in increased diffusion resistance. As seen in Fig. 5, for the lower conversion region at the maximum slope of curves, the overall reaction is chiefly controlled by the chemical reaction. On the other hand, as the conversion flattens, the overall reaction is primarily controlled by product layer diffusion. For the moderate conversion, however, both the chemical reaction and the product layer diffusion are the controlling factors. Nevertheless the comparison of the conversion curve shapes in Fig. 5 indicates that the reaction process is mainly determined by chemical reaction at temperatures above $750\text{ }^\circ\text{C}$ (Fig. 5b); the process is determined by both the chemical reaction and the product layer diffusion at $650\text{-}700\text{ }^\circ\text{C}$ (Fig. 5a).

3.3 Effect of CO_2 on the chlorination processes of CaO

The present experiments are aimed to clarify: (1) how CO_2 affects the high-temperature HCl capture behavior of calcined limestone and (2) to what extent its concentration effect will be within a proper range (4-12%). According to the results of carbonation tests, several representative temperatures are chosen to for the experimental conditions. Thus, the chlorination tests of CaO were conducted in the range of $650\text{ to }800\text{ }^\circ\text{C}$, depending on the inlet CO_2 concentration (4-12%).

The effect of CO_2 concentration on the HCl capture capacity of CaO at studied temperatures are firstly presented in Fig. 6. The results reveal that the presence of CO_2 depresses the attainable maximum conversion at $650\text{ }^\circ\text{C}$ and $700\text{ }^\circ\text{C}$, but CO_2 presence has no further effect on the

conversion degree at 800 °C. Studies on HCl bonding with other calcium-based sorbents also discovered that the presence CO₂ can lead to the lower chlorination conversion [37-39]. Besides, it is found that the result of conversion reduction is contrary to the behavior observed by Partanen *et al.* [16] at 650 °C; however, the results are similar at above 800 °C. At 750 °C, a slight reduction of CaO conversion can be noticed even though the conversion values under varied CO₂ concentrations are indistinguishable. This reduction is likely related to the aforementioned results of CaO carbonation. As mentioned earlier (Fig. 4), the carbonation processes of CaO can take place vigorously in the presence of studied CO₂ concentrations at 650 °C and 700 °C, except in the case of 4% CO₂ at 700 °C. During the CaO chlorination process, parts of the CaO are diverted to form CaCO₃. The CaCO₃ produced by this carbonation reaction has the potential to act as a HCl sorbent according to (3). However, due to the presence of high CO₂ concentration, reaction (3) may not be favored. Briefly, the occurrence of CaO carbonation possibly reduces the attainable conversion degree for CaO chlorination. Roughly all of the results in Fig. 6, except in a case of 4% CO₂ at 700 °C, can be reasonably interpreted as a consequence of CaO carbonation. At lower temperatures (400-600 °C), Mura and Lallai [22] found that the higher the temperature, the stronger the inhibiting effect of CO₂ on the HCl binding capacity of CaO. On the other hand, Wang *et al.* [40] mentioned that the presence of HCl enhances the carbonation efficiencies of limestone.

The presence of CO₂ also has another remarkable influence on the reactivity of the CaO chlorination process. It can be seen from Fig. 7 that the presence of CO₂ has a significant effect on

the time required to achieve equilibrium. In other words, the chlorination of CaO is markedly accelerated in the presence of CO₂, particularly for higher concentrations (8% and 12%) and lower temperatures (650 °C and 700 °C). From Fig. 7a and 7b, one can see that the effect of CO₂ at both 8% and 12% of the reaction time for equilibrium is roughly the same. This implies that higher CO₂ concentrations have no further enhancement on the average reaction rate. Based on the collective results of CaO chlorination in the presence and absence of CO₂, it may be concluded that the presence of CO₂ enhances the rate of chlorination process merely at 650 °C and 700 °C, compared with the case of only chlorination. Nevertheless, this benefit accompanies a slight reduction of HCl capture capacity, mainly depending on the operating temperature. These results are helpful for the practical applications of using CaO to remove HCl.

To better understand the detailed behavior of rate enhancement caused by the presence of CO₂ at 650 °C and 700 °C, it is helpful to review the conversion curves in Fig. 5 and Fig. 7. As shown in Fig. 7, the conversion increases almost linearly with time from the beginning to the middle of the reaction process, implying a thorough chemical reaction controlling regime. This also suggests a fact that the diffusion limitations caused by the formation of complex product layer, consisting of a mixture of CaCl₂ and CaCO₃, hardly affect the apparent reaction rate. The apparent reaction rate mainly depends on the intrinsic reaction rate as well as diffusivities of reactant through the product layer. Therefore, the difference of diffusion limitation leads to the variation of apparent reaction rate observed. In other words, the enhancement of reaction rate observed is due to the decrease of

diffusion resistance. Nevertheless, unlike the behavior of the reaction progressing in the presence of CO_2 , a smooth increase in conversion with the reaction progress can be noticed in Fig. 5a, and the chlorination processes are almost governed by combination of the chemical reaction and the product layer diffusion. This can be ascribed to the greater diffusion resistance caused by the formation of CaCl_2 product. For this reason, the apparent reaction rates observed in the presence of CO_2 are greater than that in the absence of CO_2 , especially for higher CO_2 concentrations as well as lower temperatures.

4. Conclusions

The effects of the presence of CO_2 and its concentrations on the chlorination of calcined commercial limestone at high temperatures were investigated in an innovated fixed-bed reactor. The repeatability of the breakthrough curves is found to be good. It is proven that, under the conditions that can lead to CaO carbonation, both the rate and extent of the CaO chlorination will be affected. The results show that the presence of CO_2 is beneficial for the reaction rates of CaO chlorination performed at 650 °C and 700 °C, compared with the case of only chlorination. Nevertheless, this benefit accompanies a slight reduction of the HCl capture capacity, but higher CO_2 concentrations have no further enhancement of the rate and the reduction of the capture capacity. Due to the less diffusion limitation caused by the formation of complex product layer, consisting of a mixture of CaCl_2 and CaCO_3 , the presence of CO_2 , in fact, enhances the apparent reaction rate of CaO

chlorination process, leading to premature reaction termination. Furthermore, the presence of CO_2 also alters the main rate-controlling regime of the CaO chlorination process.

Acknowledgments

This research was sponsored by National Science Foundation under grant NSC 101-2221-E-003

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Nomenclature

b	$[-]$	stoichiometric coefficient
$C_{i,0}$	$[\text{mol}/\text{Nm}^3]$	the inlet concentration of gas component i in the gas mixtures
$C_{i,e}$	$[\text{mol}/\text{Nm}^3]$	the outlet concentration of gas component i in the gas mixtures
$F_{i,0}$	$[\text{mol}/\text{min}]$	the inlet molar flow rate of gas components i
$N_{A,0}$	$[\text{mol}]$	the initial moles of A loaded in the reactor
$N_{i, \text{lost}}$	$[\text{mol}]$	the unreacted moles of gas component i discharging from the reactor
N_{rx}	$[\text{mol}]$	the moles of gas component i that have reacted
$N_{i, \text{total}}$	$[\text{mol}]$	the total moles of gas components i entering the reactor
ν_m	$[\text{Nm}^3/\text{min}]$	the volumetric flow rate of gas mixtures
t_{eq}	$[\text{s}]$	the reaction time required for reaching the equilibrium state
X_A	$[-]$	conversion degree of solid sorbent A

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Figure captions

Figure 1	The schematic diagram of fixed-bed reactor system.
Figure 2	The fixed-bed reactor in detail.
Figure 3	The repeatability of breakthrough curves. The experimental runs were performed three times under two conditions.
Figure 4	Carbonation tests of CaO in the presence of 4-12% CO ₂ (a) 800 °C (b) 750 °C (c) 700 °C (d) 650 °C
Figure 5	Breakthrough curves and corresponding conversion curves of chlorination process of CaO (a) 650 °C and 700 °C (b) 750-850 °C
Figure 6	Maximum capture capacity of CaO as a function of temperature and CO ₂ concentration.
Figure 7	Conversion curves for chlorination processes of CaO in the presence of 4-12% CO ₂ at temperatures ranging from 650 to 800 °C (a) CO ₂ =12% (b) CO ₂ =8% (c) CO ₂ =4%

Fig. 1 The schematic diagram of fixed-bed reactor system

Fig. 2 The fixed-bed reactor in detail

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Fig. 4 Carbonation tests of CaO in the presence of 4-12% CO₂ (a) 800 °C (b) 750 °C (c) 700 °C (d)

650 °C

Fig. 5 Breakthrough curves and corresponding conversion curves of chlorination process of CaO (a) 650 and 700 °C (b) 750-850 °C

Fig. 6 Maximum capture capacity of CaO as a function of temperature and CO₂ concentration

Fig. 7 Conversion curves for chlorination processes of CaO in the presence of 4-12% CO₂ at temperatures ranging from 650 to 800 °C (a) CO₂=12% (b) CO₂=8% (c) CO₂=4%