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CaO carbonation kinetics determined using micro-fluidized bed thermogravimetric analysis

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ABSTRACT

A micro-fluidized bed thermogravimetric analysis (MFB-TGA) method based on real-time mass measurement of solid sample inside a fluidized bed was developed. This technique was used to measure the fast reaction kinetics of CaO carbonation in calcium looping with similar characteristics of a strong mass and heat transfer in the fluidized bed reactor. The effects of particle size, temperature, and CO₂ concentration on the fast reaction kinetics of CaO carbonation were investigated. The experimental data measured upon MFB-TGA were interpreted with a K-L two-phase fluidized bed model to evaluate the effect of gas exchange between the bubble phase and the emulsion phase on the carbonation kinetics. We concluded that the kinetics of CaO carbonation measured by MFB-TGA were faster than those measured via regular TGA. The reaction rate constant (k_s) was $8.0 \times 10^{-10} \text{ m}^4/(\text{mol}\cdot\text{s})$, the activation energy of the carbonation reaction was near zero, and the reaction was first order when the CO₂ concentration was within 50 vol% (1 bar). This MFB-TGA method provides a new experimental idea and method for measuring gas–solid reaction kinetics occurring inside fluidized bed reactors.

1. Introduction

Calcium looping is a promising technology and can be widely applied in many fields, such as CO₂ capture, sorption-enhanced hydrogen production, and heat storage [1–6]. Calcium looping is based on the reversible reaction between CaO and CO₂ and is typically achieved in dual fluidized bed reactors with one bed for the carbonation of CaO and the other for the calcination of CaCO₃. Recent reviews have extensively covered the large volume of literature published to date [7,8]. The application of calcium looping requires the accurate carbonation kinetics of CaO with CO₂ for reactor design, operation, and optimization, model prediction, and CFD simulations. It is well known that the carbonation kinetics of CaO with CO₂ include two stages, i.e., a fast initial stage and a slower stage that is controlled by diffusion and occurs in the pores or in the solid product layer [9,10]. Another observed phenomenon is that increasing the temperature increases the critical conversion of CaO carbonation [11,12], and this temperature effect has been understood by the island growth mode occurring at the solid surface [13–16]. To describe the kinetic behaviors of CaO carbonation with CO₂, different gas–solid reaction models have been used, for example, the simplest apparent model [17–19], the shrinking core model [20], the grain model [21,22], the pore models [23–25] and the recently developed rate equation theory [26–30]. Regardless of the type of

model used for describing the carbonation kinetics, the model parameters must be measured based on a reliable experimental method.

To measure the carbonation reaction kinetics, there are four experimental methods. (i) The most widely used experimental method for measuring carbonation reaction kinetics is thermogravimetric analysis (TGA) in which approximately 2–10 mg sample is placed in a crucible and an isothermal experimental procedure is used to obtain carbonation data, i.e., the CO₂ is introduced into TGA apparatus after the temperature approaches the reaction temperature. Many researchers have used TGA to study this reaction, including Bhatia and Permuter [9], Grasa et al. [23], Sun et al. [31], and Kyaw et al. [32]. TGA is widely used because of its accurate and stable measurement of the real-time solid sample mass, which is a good basis for kinetics study, although possible mass and heat transfer problems are always difficult to ignore because the solid sample is in a packed state in the crucible for TGA [33,34]. Besides, different designs of the TGA apparatus can also make a difference. Despite the similar raw material and reaction conditions, the kinetic parameters obtained by TGA, namely the reaction order and activation energy, have not come to an agreement [35]. Alonso et al. [36] also studied this reaction in different TGA apparatuses and concluded that the design of the TGA oven can be a source of error. (ii) The second type of experimental method for measuring carbonation kinetics is a fluidized bed reactor with the gas concentration as a measuring

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Nomenclature

C_{b,CO_2}	concentration of CO_2 in the bubble phase, mol/m ³
C_{e,CO_2}	concentration of CO_2 in the emulsion phase, mol/m ³
$C_{e,CO_2,ave}$	average concentration of CO_2 in the emulsion phase, mol/m ³
$C_{CO_2,eq}$	equilibrium concentration of CO_2 , mol/m ³
d_b	bubble diameter, m
d_p	diameter of calcium oxide particle, m
f_a	volume fraction of CaO particle in all solid volume
I_1	the impact factor of external mass transfer
I_2	the ratio of the reaction rate in emulsion phase to the mass transfer rate from bubble to emulsion phase
K_{be}	overall gas interchange coefficient between bubble and emulsion phases, s ⁻¹
K_C	the initial reaction rate independent of CO_2 concentration, m ³ /(mol·s)
K_r	carbonation rate constant of particles in the emulsion phase, s ⁻¹
k_s	rate constant for the carbonation reaction, m ⁴ /(mol·s)
k_g	external mass transfer coefficient, m/s
M_{CaO}	molar mass of CaO, g/mol

M_{CO_2}	molar mass of CO_2 , g/mol
m_{CaO}	mass of a single calcium oxide particle, g
m_s	mass of added calcium oxide sample, g
$m(t)$	mass measured by weight transducer at time t , g
m	exponential factor in gas–solid model
Q_g	volume flow rate from the distributor to reactor outlet, m ³ /s
S_0	initial surface area of CaO per unit volume of solid particle, m ² /m ³
U_b	bubble rise velocity, m/s
U_b^*	effective gas velocity in the bubble phase, m/s
U_0	superficial gas velocity, m/s
U_{mf}	minimum fluidization velocity, m/s
V_f	volume from the distributor to the reactor outlet, m ³
X	conversion of solid particle
X_L	the final conversion of each reaction stage
z	height from the distributor, m
ε_{mf}	bed voidage at minimum fluidization
ε_0	initial porosity
τ	response time of MFB-TGA, s
δ	bubble phase fraction
ρ_{CaO}	envelope density of CaO, kg/m ³

signal [24,37–39]. Dennis and Hayhurst [37] studied this reaction using a hot fluidized bed reactor decades ago. They also concluded that the activation energy of this reaction was close to zero. Yao et al. [39] investigated this reaction in a pressurized fluidized bed reactor and obtained a higher activation energy of 48 ± 17 kJ/mol. The key feature of this kind of reactor is the creation of an isothermal reaction zone by the fluidization of the hot bed material, which is usually inert. The solid sample is added to the bed zone, mixed with the bed material, and reacted with the fluidizing gas. The vigorous motion of solid particles means good heat and mass transfer, which is a natural advantage of the fluidized bed reactor for kinetics study. Currently, kinetic analysis is mainly based on the concentration signals of the flue gas of the fluidized bed reactor [40,41]. Therefore, a gas analyzer with a high resolution, good stability, and fast response is indispensable for this method. The difficulty of this method is also related to the gas concentration measurement. The problem is that the gas concentration signal cannot be simultaneously measured when there is concentration variation inside the reactor. Therefore, when the flue gas flows to the gas analyzer, the mixing of gas species could affect the original signal and cause errors. Many researchers have focused on this problem for years and concluded that the deconvolution of the gas concentration data may help [40,42]. However, in some cases, the deconvolution

method could still fail. For example, Chuang et al. [43] from the University of Cambridge studied the oxidation reaction of Cu_2O in a fluidized bed reactor. A fast mass spectrometer was used to obtain the concentration of O_2 in the flue gas. In their experiments, it was found that when the reaction time was short, namely, within 10 s, the problem of mixing was difficult to solve by the deconvolution method. In short, the current fluidized bed reactor with the gas concentration measurement is well developed for kinetic study but this method is dependent on expensive gas analyzers. (iii) The third experimental method involves a drop tube furnace in which the sorbent particle is injected into a reaction zone from the reactor top [44], and the CO_2 concentration is measured at different locations to calculate the CaO conversion. (iv) The fourth method is a newly developed in-situ XRD method [16,22,45] in which the CaO powder is placed on a plate and analyzed by X-ray diffraction.

Carbonation during calcium looping occurs in a fluidizing state; therefore, it is necessary to obtain kinetic data from the fluidized bed reactor. Additionally, a real-time mass measurement can avoid gas sampling problems in a fluidized bed reactor. It is interesting to combine a fluidized bed reactor and thermogravimetric analysis for a carbonation kinetics study to best utilize the merits of both methods. Thus, micro-fluidized bed thermogravimetric analysis (MFB-TGA) with a

Fig. 1. (a) Schematic diagram of the MFB-TGA and (b) schematic diagram of weighing the solid particles in the fluidized bed reactor.

mass measurement resolution of 1 mg was developed in this work for kinetic study of CaO carbonation with CO₂. This method combines the good mass and heat transfer of the fluidized bed reactor with a real-time mass measurement, and a moderate amount of solid sample (~50 mg) was confirmed to produce a good experimental repeatability while minimizing the effect of mass transfer. The goals of this study were to: (1) provide detailed characteristics of the MFB-TGA method based on tests; (2) investigate the carbonation reaction under different particle sizes, temperatures, and gas partial pressures; and (3) use a fluidized bed model to interpret the experimental results and determine the kinetic parameters.

2. Experimental section

2.1. Micro-fluidized bed thermogravimetric analysis (MFB-TGA)

The micro-fluidized bed thermogravimetric analysis apparatus (shown in Fig. 1(a)) that was used in this work has been previously reported by Li et al. [46]. The apparatus consisted of a quartz reactor, an electric furnace, a gas supply system, and a measuring system. The central part of the quartz reactor was designed to be a fluidized bed with an inner diameter of 20 mm, and a porous quartz plate with a thickness of 5 mm was used as the gas distributor. The mass measurement is the core of the apparatus. The entire quartz reactor rests entirely on the weighing transducer and does not contact any part of the furnace so as not to affect the mass measurement. Fig. 1(b) shows a schematic diagram how the solid particles in the fluidized bed reactor are weighed. The fluidizing gas/reactant gas flows from the bottom and passes the gas distributor, which is a porous plate. Inert (black) particles are the main components of the fluidized bed. There is a small amount of reactant (red) particles dispersed uniformly inside the bed. The method for weighing the red particles involves weighing the entire system, which is simple and has been confirmed to be effective. The weight transducer has a measuring range of 0–1200 g and a precision of 1 mg. The mass of the reactor, the inert bed material, and reactant particles are approximately 820 g, 10 g, and 50 mg, respectively. There are two thermocouples: one for furnace temperature control and the other for measuring the bed temperature. A wireless temperature measurement module was used to measure the bed temperature to avoid unnecessary connections. In the gas supply system, newly calibrated mass flow meters were used to control the gas flow rates, and magnetic valves were used to switch the gas during the experiment, as shown in Fig. 1(a).

In a typical experiment, ~10 g of silica sand was used as the bed material, forming a bed of 21 mm in height. Isothermal experiments were conducted; therefore, the experiment always began with heating to the desired temperature under an inert fluidizing agent. When the temperature inside the reactor became stable, the calcium oxide sample was then added into the reactor from the top of the fluidized bed. For each experiment, the mass of the calcium oxide sample was ~50 mg to minimize the influence of mass transfer. After a period of time of particle heating and mixing, the reaction was initiated by switching the gas from the inert gas to the reaction gas. The composition of the reaction gas and the corresponding inert gas are listed in Table 1. In Table 1, each pair of reaction gas and inert gas have close densities, which was necessary for all experiments. The reasons for this are discussed below. The gas velocity is very important for this work. When the gas velocity is too low, the fluidization condition is not good enough. When the gas velocity is too high, the mass measurement would be quite unstable, as illustrated detailedly in our previous work [46]. Therefore for all experiments, the volumetric flow rates of the reaction gas and inert gas were set to achieve a superficial velocity of 3.5–4 U_{mf} [47]. All the experiments were conducted at atmospheric pressure. Each experiment was repeated three times to ensure reproducibility.

2.2. Materials

The calcium oxide used in these experiments was prepared from calcination of a kind of natural limestone, of which the content of CaCO₃ was higher than 99%. The raw limestone was calcined in a horizontal tube furnace at 850 °C for 30 min under a nitrogen flow of 1.5 L min⁻¹ (at 273.15 K, 1 bar). The mass of the material was recorded before and after calcination to ensure complete decomposition. After cooling down in the nitrogen flow, the fresh calcium oxide was then crushed and sieved to different sizes quickly. The produced samples were then preserved in small soft storage bags to minimize the contact time of the samples with air. Four size ranges were obtained: 150–200 μm, 250–300 μm, 600–700 μm, and 900–1000 μm. The properties of the calcium oxide samples were tested based on a sample of 150–200 μm, and they are listed in Table 2. The BET surface area was measured using an ASAP 2460 from Micromeritics. The porosity was measured using mercury intrusion porosimetry (Micromeritics, Autopore IV 9510). The envelope density was measured by an AccuPyc 1340 from Micromeritics.

The silica sand was supplied by Sinopharm Group Co. Ltd. of China. The content of SiO₂ in the sand was higher than 99.8%. The size range of the bed material was chosen to be 300–350 μm.

2.3. Data evaluation

A real-time mass signal, $m(t)$, was recorded by the weight transducer during the experiment. Therefore, the carbonation conversion of calcium oxide could be calculated from Eq. (1). In Eq. (1), $m(t_0)$ is the mass value from the weight transducer at the start of the reaction, $m(t)$ is the real-time mass value, and m_s is the mass of the added calcium oxide.

$$X(t) = \frac{m(t) - m(t_0)}{m_s} \frac{M_{CaO}}{M_{CO_2}} \quad (1)$$

3. Models

The classic model for bubbling fluidized bed proposed by Kunii and Levenspiel was adapted in this work to relate the reaction and the mass transfer between phases. Generally, the K-L model can be described by Eqs. (2) and (3), which are derived from the mass balance of CO₂ in the bubble and emulsion phase. This mass balance can be established based on the assumption that no solids are in the bubble phase.

$$-U_b^* \frac{dC_{b,CO_2}}{dz} = K_{be}(C_{b,CO_2} - C_{e,CO_2}) \quad (2)$$

$$-(1 - \delta)U_{mf} \frac{dC_{e,CO_2}}{dz} = -\delta K_{be}(C_{b,CO_2} - C_{e,CO_2}) + f_a K_r (1 - \delta)(1 - \varepsilon_{mf})(C_{e,CO_2} - C_{CO_2,eq}) \quad (3)$$

The bubble fraction can be estimated by Eq. (4), which was put forward by Abanades et al. [48] based on the theory from Kunii and Levenspiel.

$$\delta = \frac{U_0 - U_{mf}}{U_b + \frac{5U_{mf} - U_{b,eq}}{4}} \quad \text{for } 1 < \frac{U_b \varepsilon_{mf}}{U_{mf}} < 5 \quad (4)$$

The effective gas velocity (see Eq. (5)) in the bubble phase was calculated based on the gas balance in a cross section of the fluidized

Table 1

The composition of reaction gas and inert gas.

Reaction Gas	Inert Gas
15.0 vol% CO ₂ + 85.0 vol% N ₂	20.0 vol% Ar + 80.0 vol% N ₂
28.0 vol% CO ₂ + 72.0 vol% N ₂	37.8 vol% Ar + 62.2 vol% N ₂
50.0 vol% CO ₂ + 50.0 vol% N ₂	68.0 vol% Ar + 32.0 vol% N ₂

Table 2
Properties of calcined limestone.

Particle size (μm)	BET surface area (m ² g ⁻¹)	Porosity	envelope density (kg m ⁻³)
150–200	18.2	0.49	1580

bed.

$$U_b^* = \frac{U_0 - (1 - \delta)U_{mf}}{\delta} \quad (5)$$

The interchange coefficient between the bubble and emulsion phase can be estimated by Eq. (6) in this case. The calculation of the bubble diameter is included in the [supplementary material](#).

$$K_{be} = 4.5 \frac{U_{mf}}{d_b} \quad (6)$$

The only undefined parameter in Eqs. (2) and (3) is the rate constant term, K_r . The reaction was assumed to be first order according to the literature [9,23,31], and the experimental results were used later to verify this assumption. Considering the external mass transfer from the emulsion phase to the particle surface [49], K_r can then be expressed by Eq. (7).

$$K_r = \frac{1}{\frac{1}{K_{ri}} + \frac{d_p}{6k_g}} \quad (7)$$

where $K_{ri} = \frac{\rho_{CaO}}{M_{CaO}} k_s \frac{S_0}{1 - \varepsilon_0} \left(1 - \frac{X}{X_L}\right)^m$ based on the semi-empirical kinetic model proposed by Fang et al. [50]. The detailed models are included in the [supplementary material](#).

The calculation started from time zero (zero conversion) with a given rate constant, k_s . Then, the value of K_r was obtained from Eq. (7). Subsequently, the concentration profile of CO₂ in the fluidized bed was solved analytically based on Eqs. (2) and (3) to obtain the average CO₂ concentration in the emulsion phase ($C_{e,CO_2,ave}$). The details of analytical solutions are also included in the [supplementary material](#). Then, the increase in conversion of solid CaO in one time step was calculated by Eq. (8). Finally, the conversion versus time curve was obtained by the time iteration. The value of k_s was obtained by fitting the calculated curve to the experimental data.

$$dX = \frac{M_{CaO}}{\rho_{CaO}} K_r (C_{e,CO_2,ave} - C_{CO_2,eq}) \cdot dt \quad (8)$$

To understand the effect of mass transfer to the carbonation reaction in the fluidized bed, two coefficients were defined and calculated. The impact factor of the external mass transfer, which is defined as the ratio of the external mass transfer rate to the initial reaction rate, is shown in Eq. (9).

$$I_1 = \frac{\pi d_p^2 k_g}{k_s \frac{S_0}{1 - \varepsilon_0} \frac{m_{CaO}}{M_{CaO}}} \quad (9)$$

Another coefficient was defined as the ratio of the reaction rate in the emulsion phase to the mass transfer rate between the bubble phase and emulsion phase, see Eq. (10).

$$I_2 = \frac{f_a K_r (1 - \delta)(1 - \varepsilon_{mf})}{\delta K_{be}} \quad (10)$$

4. Results

4.1. Characteristics of MFB-TGA

The effect of the operational gas velocity on MFB-TGA is a very important factor that should be carefully selected. Based on our previous work [46], the apparent mass change due to the gas–solid reaction could be measured accurately if the gas velocity was controlled below a proper value, namely $6 U_{mf}$. Therefore, in this study, the gas velocity ($3.5\text{--}4 U_{mf}$) was selected for the mass measurement. Moreover, more detailed characteristics of the MFB-TGA are discussed in this paper based on our recent experimental results. The response time is defined as the time required for the system to measure the mass change of solid samples inside a reactor. The response time, τ , was determined by both the response of the weight transducer and the response of the reactor. In this work, the weight transducer recorded data every 0.2 s. Additionally, in our previous work [46], the response time of the weight transducer was confirmed to be much less than 1 s for a normal reaction. Therefore, the response of the reactor may determine the total system response time. According to the principle of MFB-TGA, when a gas–solid reaction occurs in a fluidized bed, the measured mass does not instantly change because the mass transfer between gas and solid is still an internal effect. This means that the mass change of a solid sample can be measured only when the reacted tail gas leaves the reactor. The measured mass will never change if there is no gas flow in and out after the reaction. Therefore, the time required by the reaction gas to flow from fluidized bed zone to reactor outlet is the response time of the reactor, which can be calculated by Eq. (11).

$$\tau = \frac{V_f}{Q_g} \quad (11)$$

In Eq. (11), Q_g is the volume flow rate, and V_f is the volume from the distributor to the reactor outlet. Under typical conditions, the bed temperature is 650 °C, and the volume flow rate is 1.15 L min⁻¹ (at 273.15 K, 1 bar). The calculated response time is approximately 0.80 s.

In a MFB-TGA system, gas status is an important factor that affects the mass measurement. This is because the force of the gas on the reactor is closely related to the gas state, for example, the gas type and

Fig. 2. (a) Mass change when switching between pure nitrogen and argon and (b) mass change when switching between the designed inert gas and reaction gas.

density. In this work, isothermal experiments were the focus, and the temperature did not influence the mass measurement. In a typical experiment, the fluidizing gas needs to be changed from an inert gas to a reaction gas. Therefore, it is necessary to determine how much this will affect the mass measurement. Fig. 2(a) shows the mass change results when switching between pure nitrogen and argon. This switch occurred at 650 °C, and the gas volume flow rate was still 1 L min⁻¹ (at 273.15 K, 1 bar). It can be seen that the mass change was notable because of the significant density difference in these two pure gases. We inferred that the mass change caused by the reaction would be covered if the inert gas and the reaction gas have a non-negligible density difference. Therefore, the composition of the reaction gas and corresponding inert gas were set as shown in Table 1 to eliminate the density difference. A gas switch test was designed to verify the influence of the gas compositions shown in Table 1. The test was performed at 650 °C with silica sand of 300–250 µm diameter as the bed material. The reaction gas was 15.0 vol% CO₂ with a nitrogen balance, and the inert gas was 20.0 vol% Ar with a nitrogen balance. The gas velocity was set to 3.5 U_{mf} . The gas switch was conducted by magnetic valves. The results are shown in Fig. 2(b). As shown, the mass change was almost within ± 1 mg. When switching from the inert gas to the reaction gas, the measurement was not influenced at all. Therefore, we concluded that the reaction data would not be disturbed by switching the gas, as shown in Table 1.

4.2. Typical raw data of the carbonation reaction

The real-time mass of the entire quartz reactor was recorded, which could be used to calculate the solid conversion defined by Eq. (1). Meanwhile, the pressure difference between the inlet and outlet of the reactor was measured to monitor the fluidization conditions. The results for 700 °C and 15 vol% CO₂ are shown in Fig. 3.

As shown from Fig. 3(a), the mass of the total reactor was about 820 g, whereas the mass change caused by the reaction was less than 30 mg. The notable feature of the carbonation reaction of calcium oxide is that there are obviously two reaction stages, which include a fast kinetically controlled stage and a slow diffusion-controlled stage. Fig. 3(a) clearly shows these two stages; therefore, the mass data from MFB-TGA were reasonable. As shown from Fig. 3(a), the raw mass data were not perfectly smooth with some minor fluctuations. However, this did not influence the trend of the curve, which was sufficient for analysis of the reaction kinetics. Fig. 3(b) shows that the pressure difference of the bed fluctuated around a stable value, which indicated that the reactor was operated under good fluidization conditions.

4.3. The influence of particle size

The influence of particle size is always important to understand when determining the kinetics of a gas–solid reaction because mass transfer resistance can be remarkable for large particles. Therefore, it is necessary to determine a proper particle size for kinetic experiments.

Fig. 3. (a) Mass signal and (b) pressure difference at 700 °C and 15 vol% CO₂.

Fig. 4. The carbonation conversion with different particle sizes at 650 °C and 15 vol% CO₂.

Theoretically, there is the influence from mass transfer as long as the particle size is larger than zero. Whereas under the practical circumstances, the mass transfer becomes fast enough and its resistance can be neglected for particles smaller than a certain size. In this paper, the carbonation conversion with different particle sizes is shown in Fig. 4. As shown, the conversion rate considerably increased when the particle size decreased from 900–1000 µm to 250–300 µm; it then became stable when the particle size further decreased to 150–200 µm. From the results shown in Fig. 4, it could be assumed that the carbonation reaction was almost kinetically controlled for a particle size of 150–200 µm. Therefore, the following experimental and model results are all based on this size range.

4.4. The influences of temperature and CO₂ concentration

Temperature and CO₂ partial pressure are the most important influencing factors for the carbonation reaction. In this study, all the experiments were performed at atmospheric pressure; thus, the CO₂ concentration determined its partial pressure. Fig. 5(a) shows the influence of temperature at a certain CO₂ concentration. From 600 to 700 °C, the conversion curve was clearly divided into two stages, whereas for 750 °C, this was not obvious. This may be the reason for the stronger reverse reaction at higher temperature. From 600 to 700 °C, the reaction rates in the fast stage were similar, whereas the final conversion of the first stage increased with temperature. Moreover, concerning the final conversion of the reaction, it was still much lower at 600 °C than at other temperatures. The lower conversion at 600 °C could be due to the smaller reactant layer thickness at lower temperatures, as discussed by other researchers [26,29].

Fig. 5(b) shows the carbonation conversion at different CO₂

Fig. 5. (a) Carbonation conversion at different temperatures (15 vol% CO₂) and (b) carbonation conversion at different CO₂ concentrations (650 °C).

concentrations. As shown, the final conversion of the first stage was similar for different CO₂ concentrations, which is reasonable because it was more dependent on the temperature. The reaction rate during the first stage increased with CO₂ concentration, which exhibited the characteristics of a first order reaction.

4.5. Comparison between model results and experimental data

A comparison between the experimental and model results under different conditions is shown in Fig. 6. Based on the proposed model, the kinetic parameters and mass transfer coefficients are listed in Table 3. We concluded that external mass transfer on the surface of the particle could be neglected because the external mass transfer rate was much faster than the reaction rate for all the experiments in our study.

Fig. 7(a) shows the ratio of the average CO₂ concentration in the emulsion phase to the inlet CO₂ concentration. Fig. 7(b) shows the ratio of the reaction rate in the emulsion phase to the mass transfer rate from the bubble phase to the emulsion phase. The results indicate that the amount of CO₂ consumed by the carbonation reaction should not be neglected, especially at the beginning of the reaction. The consumption of CO₂ results in a decrease in the CO₂ partial pressure and then

Table 3

Rate constant, exponential factor, and the impact factor I_1 as determined by the model.

Case	$k_g/10^{-10}$ (m ⁴ mol ⁻¹ s ⁻¹)	I_1	m	
			1st stage	2nd stage
600 °C, 15 vol% CO ₂	8.00	18.98	2/3	5/3
650 °C, 15 vol% CO ₂	8.00	20.64	2/3	5/3
650 °C, 28 vol% CO ₂	8.00	20.66	2/3	5/3
650 °C, 50 vol% CO ₂	8.00	20.73	2/3	5/3
700 °C, 15 vol% CO ₂	8.00	22.32	2/3	5/3
750 °C, 15 vol% CO ₂	3.10	62.07	2/3	5/3

influences the reaction in return. Therefore, the establishment of a fluidized bed reactor model is quite necessary to obtain accurate kinetic parameters.

5. Discussion

In the model, the reaction was assumed to be first order to obtain the expression of K_r . Fig. 6 shows that the modeled results predicted the

Fig. 6. Model vs. experimental results under different condition.

Fig. 7. (a) Ratio of the average CO₂ concentration in emulsion phase to the inlet CO₂ concentration and (b) ratio of the reaction rate in emulsion phase to the mass transfer rate from the bubble phase to the emulsion phase.

experimental results well at different CO₂ concentrations, which means that the assumption of a first order reaction is rational. In this study, the highest CO₂ concentration was 50%, which means that the reaction is first order within a CO₂ partial pressure of at least 50 kPa. This result was consistent with the results of Grasa et al. [23], who reported the reaction to be first order up to 100 kPa. However, some other researchers reported different results. For example, Sun et al. [31] and Bhatia and Perlmutter [9] considered the reaction to be first order when the CO₂ partial pressure was within 10 kPa and then zero order for higher CO₂ partial pressures. Yao et al. [39] also obtained the conclusion of a transitional CO₂ partial pressure, which they determined to be between 18.9 and 31.6 kPa in their study.

The activation energy is another important parameter concerning the kinetics of a gas–solid reaction. This carbonation reaction rate during the first reaction stage is widely reported to have a low dependence on temperature. Bhatia and Perlmutter [9], Dennis et al. [37], and Biasin et al. [16] considered this reaction to have a zero activation energy in the kinetically controlled region. Some other researchers [31,39] reported the activation energy of the rate constant to be within the range of 20–50 kJ/mol. In this study, as shown from Table 3, the value of k_s had a weak correlation with temperature for the range of 600–700 °C, which made the determination of activation energy difficult. Therefore, the activation energy of the rate constant was not calculated in this study.

The value of k_s is worth more discussion and comparison with published values. As is well known, the k_s is strongly dependent on the gas–solid kinetic model. Therefore, it is necessary to make comparisons on the same basis. In published studies by Bhatia and Perlmutter [9], Grasa et al. [23], and Yao et al. [39], the random pore model was used to obtain k_s . The random pore model is quite different from the model used in this study, but they have similar form, which is “ $dX/dt = k_s S_0 C \cdot f(X)$ ”. In both models, $f(X)$ is a mechanism function and equal to 1 when $t = 0$, and the concentration is an experimental variable. Therefore, the value of “ $k_s S_0$ ” should be the basis for a model result comparison. In some other studies, the kinetic model did not contain any term like “ $k_s S_0$ ” or the kinetic model was not used at all. Therefore, a new parameter was defined for comparison, as shown in

Eq. (12). K_C represents the initial reaction rate independent of CO₂ concentration. Apparently, this value is equivalent to “ $k_s S_0$ ” under the circumstances of our model and the random pore model. Of note, the calculation of K_C is based on the view that the carbonation reaction is first order even when the CO₂ partial pressure is as much as 100 kPa, according to the conclusion of Grasa et al. [23] and our results.

$$K_C = (dX/dt)_{t=0}/C \quad (12)$$

Table 4 shows a comparison of the rate constants at 650 °C from different studies. The reason why 650 °C was chosen were that the reverse reaction was not strong at this temperature. At a higher temperature the measured reaction rates could be pretty complex because the stronger reverse reaction. Although different experimental methods and sample amounts were used, most of the results stayed within the same order of magnitude. The most similar result is from the work of Yao et al., where the fluidized bed reactor was also used. Besides the rate constant measured by this MFB-TGA method shows an obviously higher value than that from TGA results. Comparing the two TGA results from the literature [9,23], the rate constants were similar; however, they came to different conclusions regarding the reaction order. The measured reaction rate at a high CO₂ partial pressure was much higher in the study by Grasa et al. [23] than in that by Bhatia and Perlmutter [9]. The results of Grasa et al. were obtained using a specially designed TGA with a sample in a platinum basket, and their measurement was not influenced when the CO₂ partial pressure was up to 100 kPa; thus, conventional TGA could possibly be improved further to eliminate the influence of mass transfer.

6. Conclusion

Micro-fluidized bed thermogravimetric analysis (MFB-TGA) was developed to measure the fast reaction kinetics of the CaO–CO₂ reaction in calcium looping. The real-time mass variations of a solid sample with time were directly measured, and the experimental data were analyzed with a K-L model to evaluate the effect of gas exchange between the bubble phase and the emulsion phase on the carbonation kinetics. We found that the external mass transfer around a particle is not a control

Table 4
Comparison of the rate constant for the carbonation reaction with literatures at 650 °C.

Literature	Method	Signal	Sample mass	$k_s/10^{-10}$ (m ⁴ mol ⁻¹ s ⁻¹)	$S_0/10^6$ (m ² /m ³)	$K_C/10^{-2}$ (m ³ mol ⁻¹ s ⁻¹)
This work	MFB-TGA	Mass	~50 mg	8.00	28.8	2.30
Bhatia and Perlmutter [9]	TGA	Mass	~1.3 mg	5.95	25.0	1.49
Grasa et al. [23]	TGA	Mass	2 mg	3.48	42.0	1.46
Yao et al. [39]	Fluidized bed	Gas concentration	500 mg	6.03	30.6	1.85
Turrado et al. [44]	Drop tube reactor	Gas concentration	\	\	\	0.51
Biasin et al. [45]	In situ XRD	Crystal structure	~5 mg	\	\	1.73

step if the particle size is smaller than 200 μm . With an increase in reaction temperature, CaO conversion during the fast reaction stage increases. When the carbonation reaction approaches equilibrium, a slow CaO conversion rate occurs. The experimental results under different CO_2 concentrations showed that the CaO carbonation reaction is first order within a CO_2 partial pressure of at least 50 kPa. In contrast to regular TGA results, the carbonation kinetics measured inside the MFB-TGA were faster, and the calculated apparent rate constant was $8.0 \times 10^{-10} \text{ m}^4/(\text{mol}\cdot\text{s})$ and had a weak dependence on temperature from 600 to 700 $^\circ\text{C}$. This newly developed MFB-TGA method combines the good mass and heat transfer of a fluidized bed reactor with real-time mass measurement of a solid sample, and it provides opportunities to measure fast kinetics of gas–solid reactions under fluidization conditions. This method can be used not only for the carbonation reaction of CaO but also for other gas–solid reactions.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.fuel.2019.116823>.

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