Comparison of CO₂ adsorption/desorption behaviors of a solid amine sorbent in fixed and fluidized beds

Chenhuan Xu¹, Yongmin Zhang ^{1*}, Tianlei Yang², Zhe Liu¹, Feng Qiu², Shuai Jiang²

1 State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Beijing, 102249, P. R. China

2 Beijing DERUNCHEN Environmental Protection Technology Co., Ltd, 100022, P. R. China (*Corresponding Author: zhym@cup.edu.cn)

ABSTRACT

The CO₂ adsorption and desorption behaviors, CO₂ adsorption capacity, including the CO_2 adsorption/desorption kinetics and bed pressure drops under post-combustion CO₂ capture conditions in both fluidized and fixed beds, were investigated for the first time using a solid amine sorbent in a temperature swing adsorption (TSA) experimental rig. The results show that the saturated CO₂ adsorption capacities are basically the same in fluidized and fixed beds. However, the sorbent exhibits faster adsorption and desorption kinetics in a fluidized bed, as reflected by the fitted parameters of the Avrami kinetic model and the change of bed temperature during adsorption and desorption tests. Moreover, CO₂ is not a suitable fluidizing gas in a desorber as high CO₂ partial pressure inhibits the desorption process. The bed pressure drops in fluidized beds are much lower than that in fixed beds of same sorbent mass, especially at high superficial gas velocities and high sorbent loadings. By further discussion, a fluidized bed can also achieve lower equipment investment and less sorbent loading compared to multiple fixed beds in parallel. This study demonstrates the advantages of fluidized beds over fixed beds in large-scale TSA units in view of higher reactor efficiency, lower energy consumption and equipment investment.

Keywords: solid amine sorbent, kinetics, pressure drop, fluidized bed, post-combustion CO₂ capture

Abbreviations	
CFB	Circulating fluidized bed
TSA	Temperature swing adsorption

IER	Ion exchange resin
DAC	Direct air capture
TGA	Thermogravimetric analyzer
MFB	Microfluidized bed
Symbols	
Symbols n	Fluidization number
Symbols n L/D	Fluidization number Langth to deameter ratio

1. INTRODUCTION

Carbon dioxide (CO₂) emission has been increasing rapidly over the past decades resulting in rising global concerns on climate change. Major sources of emission of CO₂ are the stationary sources such as coal-fired power plants, cement plants, oil refineries and so on [1]. Post-combustion CO₂ capture based on retrofitting the existing energy infrastructure has attracted much attention as a practical short-term solution to reduce stationary sources CO₂ emissions [2, 3]. Among various post-combustion CO₂ capture technologies, amine scrubbing using aqueous amine solutions has reached technological maturity [4]. Despite this, the technology still suffer from disadvantages like energy intensive desorption, the formation of corrosive byproducts, and requirement of large solvent makeup [5]. To overcome these shortcomings, solid amine sorbents are designed to follow similar reaction pathways as aqueous amine solutions but overcome the disadvantages mentioned above. In addition, they also have high CO₂ adsorption capacity and good selectivity in typical flue gas (<15% CO_2), so it is considered as the most promising sorbent [6-8].

[#] This is a paper for International CCUS Conference 2023 (ICCUSC2023), April 14-15, 2023, Beijing, China.

According to the preparation methods, solid amine sorbents can be classified into three classes: porous supports impregnated with amines (class 1), porous supports with amines covalently bound to oxide supports (class 2), and amines covalently bonded to polymeric supports (class 3). Among them, resin-based sorbent synthesized through in-situ polymerization was a typical kind of class 3 sorbent. Generally, ion exchange resin (IER) will be chosen as the polymeric support and then functionalized with primary amine to further react with CO_2 in the atmosphere. The main reaction between primary amine and CO_2 occurs at a relatively low temperature, with the formation of carbamate in dry conditions and bicarbonate in wet conditions:

 $2\mathrm{NH}_{2} + \mathrm{CO}_{2} \xrightarrow{30-70^{\circ}\mathrm{C}} \mathrm{RNHCOO}^{-} + \mathrm{H}^{+},$ $\mathrm{RNH}_{2} + \mathrm{CO}_{2} + \mathrm{H}_{2}\mathrm{O} \xrightarrow{30-70^{\circ}\mathrm{C}} \mathrm{RNH}_{3}^{+} + \mathrm{HCO}_{3}^{-}.$

 CO_2 is further released at higher temperatures. Resinbased sorbents quickly become potential choices for direct air capture (DAC) [9] and post-combustion CO_2 capture process [10] due to good behaviors in CO_2 capacity, kinetics and stability [11-13]. Compared with the development of novel sorbents, it is equally important to realize the CO_2 capture applications of relatively mature sorbents (such as the resin-based sorbents mentioned above) in the industrial flue gas.

Currently, several famous commercial units are polluters with the most urgent demands for flue gas CO₂ capture, which include boilers in coal fired power plants and regenerators of fluid catalytic cracking units in petroleum refineries. Huge processing capacity due to the high flue gas flowrates and uninterruptible operation is one of the major challenges to implement carbon capture based on solid amine sorbents in these units. Therefore, a circulating fluidized bed temperature swing adsorption (CFB-TSA) carbon capture process has become a widely recognized option [10, 14, 15]. As shown in Fig. 1, the process consists of at least an adsorber, a desorber and a cooler, with sorbents circulating among them in fluidization state. Among them, the adsorber and the desorber are the main places of the TSA processes. In the adsorber, sorbent selectively adsorbs CO_2 from the flue gas at $20^{\sim}70^{\circ}C$. Then, CO₂-loaded sorbent is continuously transferred to a desorber, where it is heated to >100°C to release the adsorbed CO₂. Typically, pure CO₂ and steam may be two possible fluidization gases to facilitate the downstream CO₂ liquefaction during desorption processes [16]. The successful design and operation of the adsorber and desorber requires much information on the CO₂ adsorption and desorption behaviors of the



Fig. 1. Schematic of a CFB-TSA carbon capture process

sorbents in fluidized bed. Specifically, a higher working CO_2 adsorption capacity and faster kinetics during the TSA cycles between the adsorber and desorber can make the carbon capture process technically and economically feasible [17]. The corresponding pressure drop through the sorbent bed is also a necessary guidance to estimate the capital and operating costs and to size the blowers or pumps required to force fluid through it [18].

To date, most studies on CO₂ adsorption and desorption behaviors are performed in fixed bed or thermogravimetric analyzer (TGA). For example, Choi et al [19]. and Chen et al [20]. recently used TGA to scrutinize the effects of amine structures and support structures on CO₂ adsorption and desorption kinetics. Lai et al [21]. and Liu et al [22]. evaluated the CO₂ adsorption capacity as well as adsorption and desorption kinetics of their novel developed sorbents using a fixed bed. Although they provided good comprehensions of CO₂ adsorption and desorption behavior and the effect of operating factors, the commonly acknowledged heat and mass transfer limitations that occur inside the TGA and fixed bed would underestimate the kinetics, making the obtained results difficult to direct industrial CFB-TSA carbon capture processes to a certain extent. However, few studies have been performed on the CO₂ adsorption and desorption behavior of solid amine sorbents in bench-scale fluidized bed reactors, among them Monazam et al [23]. systematically investigated CO₂ adsorption capacity and kinetics of PEI/silica sorbent in a fluidized bed by analyzing the breakthrough curves. Different from using general measuring method, Wang et al [24]. studied CO₂ adsorption kinetics of a

commercial resin-based sorbent novel by а microfluidized bed thermogravimetric analysis (MFB-TGA) method, thus obtaining fast CO₂ adsorption kinetic parameters compared with those obtained by TGA. It is obvious that the few existing studies using fluidized beds lack the investigation of the desorption performance of the sorbent, especially the desorption performance of the sorbent in commonly selected steam and CO₂ atmosphere. Moreover, there are no studies focusing on the pressure drop through the sorbent bed during adsorption and desorption processes to the best of our knowledge.

On the basis of the literature survey, we for the first time systematically investigated the CO₂ adsorption and desorption behaviors of a commercial resin-based sorbent (DRC-I) in a fluidized bed and compared them with the results obtained in a fixed bed. Before the formal experiment, we first obtained the minimum fluidization velocities of the sorbent under various operation conditions involved in the adsorption and desorption experiment (Section 2.3). Then comes the four main contents: (1) measurement of saturated CO₂ adsorption capacity of the sorbent in different CO₂ concentration and temperature (Section 3.1); (2) investigation of CO₂ adsorption kinetics of DRC-I in different adsorption temperature (Section 3.2); (3) investigation of CO₂ desorption kinetics using CO₂ and N₂ as stripping gases in different desorption temperature (Section 3.3). (4) measurement of pressure drops through the sorbent bed in different superficial gas velocities (Section 3.4). According to the investigation and comparison of the above four aspects, we finally put forward further discussions on the reactor design and desorption strategies of large-scale CFB-TSA carbon capture processes (Section 3.5).

2. EXPERIMENTAL SECTIONS

2.1 Material

The resin-based sorbent (DRC-I) used in this study was supplied by Beijing DERUNCHEN Environmental Protection Technology Co., Ltd. It is a commercial solid amine sorbent synthesized by an in-situ polymerisation method, where polystyrene-divinylbenzene copolymer was functionalized with amino-methylene groups through an amide alkylation reaction. Based on this method, an amino-methylene porous polymer, functionalized with a primary amino group, was obtained. The particle size distribution (Fig. 2) of the sorbent were measured by a Bettersize 2600 (Dandong Bettersize, CHN). The bulk density of the sorbent is 480

kg/m³, which was obtained by dividing the mass of the sorbent by the volume occupied by the sorbent [25]. The specific pore volume and pore size distribution of the sorbent was measured by AutoPore V 9600 (Micromeritic, USA) using mercury intrusion method. As shown in **Fig. 3**, the specific pore volume is 0.43 cm³/g and the pore sizes are in the range of 20~150 nm, indicating that macroporous structures account for the majority. True density was measured by AccuPyc II 1340 (Micromeritic, USA). The particle density was calculated to be 714.7 kg/m³, according to the results from **Fig. 3** and true density. Based on the particle size and density, the sorbent particle is categorized in Geldart's group B. The relevant physical parameters are summarized in **Tbl. 1**.



Fig. 2. Cumulative and differential particle size distributions of DRC-I



DRC-I

Tbl. 1. Physical properties of DRC-I					
Physical Properties	Unit	Value			
Average particle size	μm	571.5			
Bulk density	kg/m ³	480.3			
Particle density	kg/m ³	714.7			

True density	kg/m ³	1176.1
Attrition index	%/h	0.05
Geldart's classification [26]	-	Group B

2.2 Experimental rig

The study of CO₂ adsorption and desorption behaviors as well as pressure drops of the sorbent were performed in a bench-scale TSA rig as illustrated in Fig. 4. Feed gases (N₂ and CO₂) were provided from highpurity (99.999%) cylinders and transmitted to the preheater with separate mass flow controllers (MFC). In order to get closer to the industrial processes, feed gases will be preheated to the same temperature as the reactor before entering the reactor. The reactor together with sorbent were heated by the heating jacket and the temperature was controlled by type K thermocouples. Specifically, the reactor, 150 mm in height and 20 mm in diameter, has a gas distributor and two branch pipes. A u-tube manometer was connected to the two branch pipes on the reactor to monitor the pressure drop of the sorbent bed (ΔP). CO₂ composition of the outlet stream was continuously recorded by an online infrared (IR) analyzer (Testo, Germany, measurement limit 0-50 vol%).

Moreover, when operating in fluidized bed conditions, feed gases were blown through the reactor from bottom to top (Type A). Conversely, when experiments were performed in fixed-bed conditions, feed gases passed through the reactor from top to bottom (Type B).



(1. CO_2 cylinder; 2. N_2 cylinder; 3'/3". MFCs; 4. preheater; 5. heating jacket; 6. reactor; 7. U-tube manometer; 8. IR gas analyzer;)

Fig. 4. Schematic diagram of experimental TSA rig

2.3 Measurement of minimum fluidization velocities

In order to preliminarily obtain the fluidization characteristics of the sorbent and provide support for the formal experiments in the following sections, minimum fluidization velocity (u_{mf}) of the sorbent was measured in various CO₂ adsorption and desorption operating conditions. Pressure drops were noted for the superficial gas velocity (u_g) covering both the fixed and fluidized bed regimes in different CO₂ concentration (0%, 15%, 50%, 100%) of the feed gases and temperature (30°C, 50°C, 70°C, 60°C, 100°C, 120°C).

Fig. 5(a) and (b) exhibit the variation of pressure drop of the sorbent bed as a function of increasing superficial gas velocity. Pressure drop increases linearly with the superficial gas velocity (u_g) when sorbent bed is fixed, this behavior can be explained by Ergun's equation [27]. Since in the present work the particle Reynolds numbers are always less than 10, the simplified Ergun's equation can be expressed as Equation (1), where pressure drop is linearly proportional to superficial gas velocity. As the superficial gas velocity increases gradually, the pressure drops then levelled off irrespective of further increase in superficial gas velocity when the sorbent bed is fully fluidized. The transition point of superficial gas velocity between fixed bed and fluidized bed corresponds to the minimum fluidization velocity. When minimum fluidization velocity is achieved, small smooth bubbles are observed directly without significant bed expansion in this study, again demonstrating that the sorbent belongs to Geldart B particle.

$$\frac{\Delta p}{H} = \frac{150\mu_g u_g \left(1-\varepsilon\right)^2}{\phi_s^2 d_p^2 \varepsilon^3} \tag{1}$$

Moreover, it can be seen from **Fig. 5(a)** that the minimum fluidization velocity decreases with the increasing CO₂ concentration of the feed gasses. Since the viscosity (μ_g) of the feed gases decreases with the increasing CO₂ concentration, the drag force of the feed gases on the sorbent particles decreases accordingly. Therefore, a higher minimum fluidization velocity is needed. Similarly, viscosity of the feed gases increases with the increasing temperature, resulting in a higher minimum fluidization velocity (**Fig. 5(b)**). However, the pressure drop in the final fluidization region keeps constant in all CO₂ concentration and temperature conditions due to its dependency only on the weight of the sorbent particle.

Summary of minimum fluidization velocities under all the adsorption and desorption conditions used in subsequent sections are shown in **Fig. 5(c)**. Different from CO_2 adsorption experiment, the CO_2 desorption experiment was performed using static weighing method [22, 28]. About 12 g of the sorbent was desorbed and weighed (m_0) prior to conducting the adsorption process. The sorbent was then adsorbed



Fig. 5. Effect of CO₂ concentration (a) and temperature (b) on pressure drop and the summary of minimum fluidization velocities (c)

2.4 CO₂ adsorption and desorption experiment

During CO₂ adsorption experiment, about 12 g of the sorbent was loaded into the reactor (L/D~4). First, N₂ was flowed through the reactor at 1 L/min while the bed temperature was raised to 120°C for 1.5 h, after which it was lowed back to the desired adsorption temperature (i.e. 30°C, 50°C, 70°C) and held for 5 min to gain the baseline of CO2. Subsequently, CO2 was added into the reactor in order to obtain the feed gases with a certain CO₂ concentration (i.e. 5%, 15%, 30%, 50%). The CO_2 adsorption experiment was finished when the CO_2 concentration of the outlet stream equals the CO₂ concentration of feed gases. The CO₂ concentration of the outlet stream throughout the adsorption process is recorded as the breakthrough curve. The amount of CO₂ adsorbed per mass of sorbent at any time Q_t (mg/g) of the sorbent was calculated by the integration of the breakthrough curves, as shown by Equation (2). All the CO₂ adsorption experiment were performed both in fixed bed and fluidized bed, with the fluidization number (n) of 2.

$$Q_{t} = \frac{44}{m_{0}} \cdot \frac{1}{V_{m}} \cdot \frac{T_{0}}{T} \cdot V \cdot \int_{0}^{t} (C_{i} - C_{o}) dt$$
 (2)

where m_0 is the weight of desorbed sorbent, g; V is flow rate of the feed gas, mL/min; C_i and C_o are CO_2 concentrations of feed gas and outlet gas, %; t denotes time, min; T_0 is 273 K and T is the adsorption temperature, K; V_m is 22.4 mL/mmol. The saturation CO_2 capacity Q_s (mg/g) is calculated at the saturation time when C_o is equal to C_i . saturated in 15% CO₂/N₂ (m_s) at 50°C, and the saturated sorbent was weighed as m_s . The sorbent was then rapidly heated to the desired desorption temperature (80°C, 100°C, 120°C), and the sorbent (m_t) together with the reactor were weighed together every 5 min by an analytical balance together with (Mettler Toledo, CH). The amount of CO₂ adsorbed per mass of the sorbent (Q_t) can be calculated as **Equation 3**. The sorbent is completely desorbed when there is no obvious change in weight of two consecutive weighing.

$$Q_{t}(mg/g) = \frac{m_{s}(g) - m_{t}(g)}{m_{0}(g)} \times 1000$$
 (3)

Typically, pure CO_2 and steam may good choices for fluidization gases in view of easiness of handling in CO_2 liquefaction [16] after desorption process. However, we found that when steam was selected as the stripping gas, it might cause the condensation of steam in the reactor, which deteriorates the fluidization quality and increases pressure drop of the sorbent bed. So we chose pure N₂, which plays a similar role in reducing the partial pressure of CO_2 as steam, as a substitute during desorption process.

The temperatures at the centre of the sorbent bed during adsorption and desorption experiments we measured by a thermocouple and recorded every two minutes.

2.5 Kinetic models

The Avrami model has been generally used to quantitatively describe the CO_2 adsorption and desorption kinetics of amine-modified materials [21, 22, 29, 30]. In this study, the Avrami model in adsorption

and desorption processes is expressed as Equation (4) and (5), respectively.

$$Q_{\rm t} = Q_{\rm e} \left(1 - e^{-(k_{\rm a}t)^{n_{\rm a}}} \right)$$
 (4)

$$Q_{\rm t} = 1 - e^{-(k_{\rm a} \cdot t)^{n_{\rm a}}}$$
(5)

Where Q_t and Q_e represent the amount of CO₂ adsorbed at any time t and equilibrium time, mg/g; k_a is the Avrami rate constant for both adsorption and desorption processes, 1/min; n_a is the Avrami exponents for both adsorption and desorption processes.

3. RESULTS AND DISCUSSIONS

3.1 CO₂ adsorption capacity:fixed vs fluidized bed

Saturated CO₂ adsorption capacity (Q_s) is one of the most fundamental evaluation parameters of a novel sorbent. **Fig. 6** shows the Q_s of DRC-I over a wide range of CO₂ concentration and temperature obtained both in a fluidized bed and a fixed bed. Firstly, Q_s obtained in fluidized bed and fixed bed are basically the same. Taking the results obtained in a fluidized bed as example, we further analyse the variation of Q_s with



Fig. 6. Q_s of DRC-I measured in fluidized bed and fixed bed: (a) at 50°C in different CO₂ concentrations; (b) at different temperatures in 15% CO₂/85% N₂

CO₂ concentration and temperature.

As shown in **Fig. 6(a)**, at 50°C in different CO_2 concentrations, Q_s of DRC-I first increases largely from 86.7~116.5 mg/g as the CO_2 concentration increases from 5~15 % and then increases slowly as the CO_2 concentration further increases from 15~50%. The results indicates that the sorbent may be more suitable for CO_2 capture in the flue gas with CO_2 concentration of about 15%.

The effect of temperature on Q_s is shown in **Fig.** 6(b), where Q_s exhibits a monotonic decrease trend with the increasing temperature (i.e. 30, 50 and 70°C). This is different from most amine impregnated sorbents, whose Qs is affected by both kinetics and thermodynamics with the increasing temperature [22, 31]. For DRC-I in this study, pore structures on the sorbent surface are mostly composed of macropores (see Fig. 2), and the amine content is moderate, so that CO2 molecules didn't need to overcome the diffusion resistance of amine modified pore structure before they approach to the active adsorption sites. At this time, thermodynamics rather than kinetics would dominate the adsorption process. So Q_s would decrease when a higher temperature is applied, owing to the exothermic characteristics.

3.2 CO₂ adsorption kinetics: fixed vs fluidized bed

Fig. 7 presents the amount of CO_2 adsorbed by DRC-I at various adsorption temperatures (i.e. 30, 50 and 70°C) and corresponding fit with the Avrami model introduced in **Section 2.5**. The approximated values of the model parameters and corresponding coefficients



Fig. 7. Experimental CO₂ adsorption kinetics data and corresponding fit with the Avrami model of DRC-I in fixed and fluidized bed

(>0.99) are listed in Table 2.

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Tbl. 2. Avrami kinetic parameters for CO ₂ adsorption and desorption of DRC-I in fixed and fluidized bed									
A. 1	Temperature	Fluidized bed				Fixed bed			
Atmosphere	(°C)	Qe	ka	n _a	R ²	Qe	ka	n _a	R ²
Adsorption in 15% $CO_2/85\% N_2$	30	135.35	1.15	0.89	0.994	132.91	0.78	0.75	0.994
	50	109.07	1.44	0.84	0.996	107.71	1.33	0.63	0.991
	70	92.12	1.26	0.51	0.991	90.32	1.26	0.51	0.990
Desorption in CO ₂	80	116.47	0.02	0.39	0.981	115.54	0.01	0.52	0.992
	100	117.05	0.03	0.41	0.987	117.13	0.02	0.46	0.984
	120	116.73	0.06	0.38	0.992	115.87	0.04	0.52	0.992
Desorption in N ₂	80	116.35	0.14	0.61	0.982	116.59	0.08	0.85	0.997
	100	115.60	0.23	1.17	0.999	116.24	0.17	1.37	0.988
	120	116.59	0.33	1.18	0.999	116.59	0.33	1.18	0.999

As the temperature increases, it can be seen in Fig. 7 that the CO₂ adsorption processes are fastened due to enhanced kinetics, but a lower amount of CO₂ adsorbed at saturation due thermodynamics, which are common in other papers [21, 32]. This can also be reflected from the Avrami rate constant k_a and equilibrium CO₂ adsorption capacity (Q_e) listed in **Table 2**. Furthermore, with the temperature increases from 30~50°C, the Avrami exponent n_a decreases both in fluidized and bed, indicating that the proportion fixed of chemisorption is lower decreases with increasing temperature [32].

Next, the difference in CO₂ adsorption kinetics of the sorbent in fluidized bed and fixed bed was compared emphatically. It can be seen from both Fig. 7 and Table 2 that even at the same superficial gas velocity, the adsorption process in a fluidized bed is faster than that in a fixed bed, especially during the initial stage. This is due to higher mass and heat transfer rate of the sorbent and feed gases in the fluidized bed. Moreover, an interesting phenomenon is that the value of $k_{\rm a}$ in the fluidized bed and the fixed bed differs greatly at lower adsorption temperatures (i.e. a difference of 0.37 at 30°C), but with the increasing adsorption temperature, the difference of k_a in fluidized bed and fixed bed decreases gradually and finally disappears at 70°C. This may due to the temperature has a greater influence on the CO₂ adsorption rate of the sorbent than the fluidization state. As the temperature increases, the CO₂ adsorption rate of the sorbent increases to a relatively high level, at which point the increase in the mass and heat transfer rate



Fig. 8. Bed temperature variation of the fluidized bed and fixed bed during CO₂ adsorption in different temperatures

due to the fluidization of the sorbent bed becomes insignificant.

Fig. 8 shows the change of bed temperature at the above adsorption processes in both fluidized bed and fixed bed. Overall, the CO₂ adsorption process is obvious exothermic. In the adsorption temperature range of 30~70°C, the maximum temperature rise (ΔT_{max}) in the fluidized bed is 31.2~16.7°C, which is more dramatic than 27.4~10.2°C in the fixed bed. This is also due to the faster adsorption process in a fluidized bed than that in a fixed bed, and the faster adsorption process results in a faster heat release. In addition, taking the results in the fluidized bed as an example, $\Delta T_{\rm max}$ before and after the adsorption decreases from 31.2°C to 16.7°C with the increase of the adsorption temperature from $30^{\sim}70^{\circ}$ C. This is because Q_{e} decreases with temperature due to thermodynamics

control, and the amount of the heat released are positively correlated with the amount of CO₂ adsorbed by the sorbent during adsorption process. Therefore, the increase of the adsorption temperature eventually leads to the decrease in the bed temperature rise. However, the bed temperatures sometimes rise more than 30°C. An increase in the adsorption temperature will reduce the CO₂ adsorption capacity of the sorbent due to thermodynamic limitation, which is undesirable. Therefore, it is necessary to install heat exchangers in the adsorber to take away the heat of adsorption to precisely control the adsorption temperature. In terms of higher precision bed temperature control in both adsorbers and desorbers, fluidized beds also hold the advantages over fixed beds, especially when loaded with large amounts of porous solid amine sorbents with low heat transfer efficiency. This is mainly due to the more uniform bed temperature and higher heat transfer efficiency in fluidized beds than those in fixed beds.

3.3 CO₂ desorption kinetics: fixed vs fluidized bed

Fig. 9 presents the amount of CO_2 adsorbed by DRC-I in fluidized and fixed bed using CO_2 and N_2 as stripping gases at various desorption temperatures (i.e. 80, 100 and 120°C). The experimental data was also fitted with the Avrami model introduced in **Section 2.5**. The approximated values of the model parameters and



corresponding coefficients (>0.98) are listed in Table 2.

As the time increases, it is also evident in **Fig. 9** that the amount CO_2 desorbed and the corresponding desorption rate increases with temperature. The increasing trend of Avrami rate constant k_a also confirm the desorption kinetics is favored with the increasing temperature. This is because the CO_2 desorption process is endothermic, the increase of desorption temperature can not only accelerate the desorption rate, but also promote the desorption degree.

Further, desorption processes using CO_2 and N_2 were analyzed. It is obvious that the desorption curves obtained in N_2 (Fig. 9(b)) are steeper than that in CO_2 (Fig. 9(a)), which means faster desorption rate, larger amount of CO₂ desorbed and less time required to complete desorption. Higher values of k_a under N₂ in Table 2 also demonstrate faster desorption rates than that under CO₂. This is because when CO₂ is selected as fluidizing gas during desorption process, the high CO₂ partial pressure in the reactor will inhibit the desorption process due to Le Chatelier's principle. Conversely, N2 can reduce the CO₂ partial pressure in the reactor so as to promote the desorption process. Furthermore, the Avrami exponent n_a lies in the range of 0.61~1.37 when N₂ is used as fluidizing gas, which is larger than 0.39~0.52 when CO₂ is used as fluidizing gas. This is because chemical desorption accounts for a larger proportion when in N₂ atmosphere than that in CO₂ atmosphere [33].

The difference in CO₂ desorption kinetics of the sorbent in fluidized bed and fixed bed was also compared emphatically. As shown in Fig. 9, even at the same superficial gas velocity, the desorption rate of the sorbent is faster in a fluidized bed than that in a fixed bed using either N₂ or CO₂ as a fluidizing gas, which can be also confirmed by k_a in **Table 2**. To explore the reason why the fluidized bed has a faster desorption rate than the fixed bed, the temperature change of the adsorbent bed during the desorption process were measured and shown in Figure 10. As the sorbent heated from room temperature to a higher desorption temperature during the desorption process, the temperature rise rate of the sorbent in the fluidized bed is faster than that in the fixed bed during desorption processes, especially at lower desorption temperatures (i.e. 80 and 100°C). Because when the sorbent is heated in a fixed bed, the wall-type heating of the reactor makes the temperature of the sorbent close to the heating wall rises rapidly, and may even cause local overheating, while the temperature of the sorbent far

Fig. 9. Experimental CO_2 desorption kinetics data and corresponding fit with the Avrami model of DRC-I when desorbed in CO_2 (a) and N_2 (b) in fixed and fluidized bed

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Fig. 10. Comparison of pressure drops in fluidized bed and fixed bed

away from the heated wall rises slowly. On the contrary, the temperature of the sorbent in a fluidized bed is more uniform, which can increase the rise rate of the temperature bed to a certain extent. The faster rise rate of the bed temperature directly accelerates the desorption rate of the sorbent.

3.4 Bed pressure drop: fixed vs fluidized bed

The pressure drop of the sorbent bed is an important parameter for reactor design, selection of blowers, and estimation of operation cost. As shown in Fig. 11, pressure drops of the sorbent bed in fluidized bed and fixed bed show different trends with the increase of the fluidization number (n). In a fluidized bed, the bed pressure drop of the sorbent bed will not increase with the increasing fluidization number. In a fixed bed, however, the pressure drop of the sorbent bed increases approximately linearly with the fluidization number. What's more, as the length to diameter ratio (L/D) of the sorbent bed increases, the difference in bed pressure drops between fixed and fluidized beds increases with the fluidization number. The above conclusions show that for adsorbers and desorbers with large sorbent loading, the use of



fluidized beds can ensure lower bed pressure drops than that of fixed beds, especially for adsorbers that have to deal with a large amount of flue gas.

3.5 Further discussions for industrial scale-up process

Based on the results and related analyses in **Section 3.1~3.4**, the reactor design and desorption strategies involved in the industrial scale-up process are further discussed.

3.5.1 Reactor design

Firstly, from the adsorption and desorption kinetic results in Section 3.1~3.2, the adsorption and desorption rates of the sorbent in a fluidized bed are still faster than those in a fixed bed even if performed in a lab-scale reactor. The advantage of fluidized bed in terms of higher reactor efficiency will be more highlighted later in scaled-up industrial reactors. Secondly, as shown in Fig. 11, no matter for adsorbers with large superficial gas velocities or desorbers with relatively small superficial gas velocities, the bed pressure drops of a fluidized bed are significantly lower than those of a fixed bed of the same specification, so the fluidized bed reactor has the potential of lower energy consumption. Thirdly, beyond the results exhibited in this paper, it is well known that when a fixed bed reactor is selected for the TSA carbon capture process, the sorbent often needs to complete the adsorption, heating, desorption and cooling processes sequentially in a single cycle, which takes a long time. So multiple fixed-bed reactors are usually conFig.d to work in parallel, which not only increases equipment investment, but also greatly increases the sorbent loading in the reactor. However, when fluidized bed reactors are selected for the TSA carbon capture process (See Fig. 1), the sorbent can simultaneously complete the adsorption, heating, desorption and cooling processes within at least an adsorber, a desorber and a cooler, thus greatly reducing the equipment investment and sorbent loading.

Therefore, compared with fixed bed reactors, choosing fluidized bed reactors as adsorbers and desorbers is more conducive to realizing higher reactor efficiency, lower energy consumption and lower equipment investment in the post-combustion CO_2 capture processes.

Fig. 11. Comparison of pressure drops in fluidized bed and fixed bed



Fig. 12. Working CO₂ adsorption capacity of the sorbent under different adsorption and desorption conditions

3.5.2 Desorption strategies

In industrial carbon capture process, the adsorption process is mainly determined by the conditions of flue gas (i.e. temperature and CO₂ concentration). Choosing a suitable desorption strategy is therefore the guarantee of high efficiency and energy saving in the whole carbon capture process. Working CO₂ adsorption capacity (Q_w) corresponds to the actual amount of CO_2 that can be captured during а full adsorption/desorption cycle and is thus a critically important parameter in evaluating the potential of a novel sorbent in a real process [34], it can be also used to explore appliable desorption strategies. When capturing an equal amount of CO_2 , a higher Q_w means fewer TSA cycles, which helps reduce the energy consumption. In this study, Q_w can be calculated as the difference between the amount of CO₂ adsorbed at saturation under specific adsorption conditions (Q_{ads}) and desorption conditions (Q_{des}) , as shown in Equation (6). Q_{ads} and Q_{des} are from the results in the fluidized bed in Fig. 7 and Fig. 9, respectively.

$$Q_{\rm w} = Q_{\rm ads} - Q_{\rm des} \tag{6}$$

As shown in **Fig. 13**, when desorbed in CO₂, the Q_w of the sorbent is on average 51.3% lower than that desorbed in N₂, which is due to the desorption degree of the sorbent in CO₂ atmosphere is much lower than that under N₂ atmosphere, as described in **Section 3.3**. More so, As the adsorption temperature decreases, Q_w will increase accordingly. Therefore, reducing the flue gas temperature properly before the flue gas enters the adsorber is also conducive to reducing energy consumption. It is obviously that the sorbent is apparently desorbed completely at 100°C in N₂ atmosphere. In this case, further increasing the desorption temperature will not increase Q_w , but will

shorten the time required for desorption due to faster kinetics at higher temperatures. The time required for desorption is therefore studied next.

Here, the time required to desorb 95% of the adsorbed CO_2 (t_{95}) is used to evaluate the time required for desorption at different desorption temperatures and fluidizing gases (adsorption at 50°C in 15% CO₂/N₂). As shown in Fig. 13, when desorbed in N₂, t₉₅ is generally much shorter than that in CO₂, which is consistent with the results in Section 3.3 that the sorbent has faster desorption kinetics in N_2 than that in CO_2 . As the desorption temperature increases, the t_{95} obtained in N₂ first decreases significantly from 17.43 to 7.19 min as the desorption temperature increases from 80 to 100°C, and then remains basically the same as the desorption temperature continues to increase from 100 to 120°C. Therefore, a desorption temperature of 100°C is enough when using N₂ as fluidizing gas. However, when desorbed in CO₂, the t_{95} only slightly reduced from 26.41 to 24.31 min, which are much longer than that



Fig. 13. Time required for the sorbent to reach 95% of tota desorption capacity

desorbed in N₂.

In summary, CO₂ is not a suitable fluidizing gas in the desorber as the high CO₂ partial pressure inhibits the desorption process, and N₂ appears to be a superior fluidizing gas during laboratory desorption. However N₂ is seldom used as a fluidizing gas in industrial processes due to the high cost and difficulty in achieving the enrichment of high-purity CO₂. Therefore, it can be deduced that steam is an ideal fluidizing gas which can not only reduce the partial pressure of CO₂ in the desorber, but also realize the enrichment of high-purity CO₂ through simple condensation. However, it also should be noted that when steam is used as fluidizing gas, it is necessary to investigate whether there exist serious steam condensation and particle agglomeration, which will be harmful to fluidization guality and the smooth operation of the CFB-TSA carbon capture unit. This part of work is going to be done in future.

4. CONCLUSION

For the first time, this study investigated and compared the CO_2 adsorption and desorption behaviors of a resin-based sorbent (DRC-I) in both fluidized bed and fixed bed reactors. The following major conclusions can be drawn:

1. The saturated CO_2 adsorption capacities measured in a fluidized bed and a fixed bed are basically the same under the same conditions. However, the sorbent exhibits faster CO_2 adsorption and desorption kinetics in a fluidized bed than that in a fixed bed, as reflected by the fitted parameters of the Avrami kinetic model and the change of bed temperature during adsorption and desorption tests.

2. CO_2 is not a suitable fluidizing gas in a desorber as the high CO_2 partial pressure inhibits the desorption process. On the contrary, steam is an ideal fluidizing gas which can not only reduce the partial pressure of CO_2 in the desorber, but also realize the enrichment of highpurity CO_2 .

3. Bed pressure drops of the sorbent in the fluidized bed is much lower than that in a fixed bed under the same superficial gas velocities, especially at high superficial gas velocities and high sorbent loadings, indicating lower energy consumptions of fluidized-bed adsorbers and desorbers when dealing with a huge amount of flue gas.

4. It is also necessary to install heat exchangers in the adsorber to take away the heat of adsorption, so as to precisely control the adsorption temperature. Fluidized beds can achieve more precise bed temperature control than fixed beds. This study demonstrates the advantages of fluidized beds over fixed beds in large-scale TSA units in view of higher reactor efficiency, lower energy consumption and lower equipment investment.

ACKNOWLEDGEMENT

The authors acknowledge financial support by the National Natural Science Foundation of China (21276273) and the Science Foundation of China University of Petroleum, Beijing (2462015YQ0312 and C201606).

DECLARATION OF INTEREST STATEMENT

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. All authors read and approved the final manuscript.

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