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CO₂ Absorption Behavior with a Novel Random Packing: Super Mini Ring

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Abstract: For the purpose of capturing CO₂ from flue gas the absorption of CO₂ into an aqueous solution of monoethanolamine was measured by using a column packed with a novel packing, Super Mini Ring (SMR). The SMR gave a higher absorption performance relative to pall ring packing due to a larger effective surface area and also reduced the frictional pressure gradient. The absorption mechanism was observed to be mainly gas phase controlling. It was concluded that for the treatment of flue gas the SMR packing could reduce the height of the absorption column by 20% relative to a pall ring packed column.

Keywords: CO₂ absorption, carbon capture, MEA, random packing, super mini ring

INTRODUCTION

Chemical absorption of carbon dioxide from gas streams is an important industrial operation and has more recently been considered as a mechanism to control greenhouse gas emissions from power stations. Many research workers have been actively addressing the capture of this greenhouse gas from flue gases

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and a range of alternative separation methods have been proposed including adsorption and membrane separation. However, the chemical absorption process is the only method that is commercially proven and numerous absorption plants are in use in many countries. To this end, the chemical absorbent must have a large capacity for CO₂, be highly selective, recoverable, and in some cases it must also have an ability to absorb other acid gases such as SO_x and NO_x. Aqueous solutions of alkanolamines can satisfy these requirements and have become the most popular and effective chemical absorbents to remove CO₂ in industry. The alkanolamines, originally discovered by Robert Roger Bottoms (1, 2) can be classified into three categories; primary, secondary, and tertiary amines. Among these alkanolamines, monoethanolamine (MEA) is the most popular solvent due to its high reactivity with CO₂.

Significant effort has been devoted not only to finding an effective solvent but to developing a highly efficient contactor. A packed column is common and both random and structured packing have been considered. It has been shown that structured packing allows for a shorter contactor relative to random packing (3). The hydrodynamic and mass transfer behavior in a structured packed column has been analyzed to give assistance for developing a new geometric feature of the packing (4). A column with structured packing, KP-1 packing developed by Mitsubishi Heavy Industries Ltd., could attain 20% higher effective surface area and 1.5 times higher gas velocity in column, relative to the absorption by CMR random packing (5). It was presented as advantages for random packing that a column with random packing could show a higher efficiency with larger liquid load absorption (6). Many researchers have been also engaged in the development and analysis of novel random packings. For example, it has been recognized recently that for high efficiency random packing the ratio of height to diameter of a ring packing has a significant influence (7) and packings with low aspect ratio have been developed (8, 9). A new packing, raschig super-ring, was developed to show higher separation efficiency relative to the structured packing, Mellapak, with a comparable surface area (10). The choice of contactor type therefore still requires careful consideration and judgment to meet the complicated demands.

This work considers the Super Mini Ring (SMR) as a novel random packing material. This ring structure was developed to meet the increasing demands of process intensification (8). Figure 1 shows the appearance of the SMR. The aspect ratio of this packing is designed to be 0.35 and its diameter and height are 13 mm and 4.5 mm, respectively. These kinds of packing with low aspect ratio can enhance the mass transfer rate and it has already been affirmed that this packing gives high efficiency for liquid-liquid extraction, decreasing pressure drop in the column, increasing specific surface area, and enhancing the surface renewal (11).

This paper deals with CO₂ absorption into an aqueous solution of 20 wt% MEA ($3.3 \times 10^3 \text{ mol} \cdot \text{m}^{-3}$) using both the novel packing, SMR, and standard pall rings. A whole series of research have been presented on investigations of operating parameters for MEA absorption (12–15). The effects of MEA



Figure 1. Appearance of Super Mini Ring (SMR).

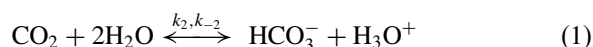
concentrations on the overall mass transfer coefficient have been measured to show many MEA plants have been operating with solution concentrations of $3.0 \times 10^3 \text{ mol} \cdot \text{m}^{-3}$ (16, 17) and it was reported that some plants have started operating at concentrations of $5.0 \times 10^3 \text{ mol} \cdot \text{m}^{-3}$. In another study, absorption experiments were conducted over the range from $3.0 \times 10^3 \text{ mol} \cdot \text{m}^{-3}$ to $9.0 \times 10^3 \text{ mol} \cdot \text{m}^{-3}$ to analyze the effects of the MEA concentration on the CO₂ absorption rates (3). The value of the overall mass transfer coefficient increases with an increase in the MEA concentration and the value starts to decrease as the concentrations exceed roughly $4.0 \times 10^3 \text{ mol} \cdot \text{m}^{-3}$ because of higher concentration making the viscosity higher. As just described the higher MEA concentration is getting popular but the higher concentration solutions simultaneously show their disadvantages. For this work the MEA concentration is selected to be 20wt% ($3.3 \times 10^3 \text{ mol} \cdot \text{m}^{-3}$), which might be able to give higher mass transfer coefficient and the CO₂ absorption performance was measured. A mass transfer model is developed to characterize the novel packing and the performance assessed by a simple case study of the CO₂ recovery process.

ABSORPTION OF CO₂ INTO MEA SOLUTION

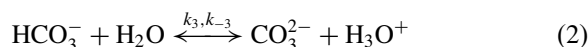
Reactions in MEA Solution

For the reactions between CO₂ and MEA in solution two reaction mechanisms are widely accepted; the zwitterion mechanism (18), developed for CO₂ absorption (19), and the termolecular mechanism (20). In this study the zwitterion mechanism is employed to express the reaction between CO₂ and MEA to form carbamate. In this case, reaction is considered to include the following reactions:

a) dissociation of dissolved CO₂ into bicarbonate:



b) dissociation of bicarbonate:



c) zwitterion formation from MEA and CO_2 reaction:



d) carbamate formation by deprotonation of the zwitterion:



here B_i stands for a basic species i ; RNH_2 , H_2O or OH^- . For this mechanism an overall forward reaction rate equation can be derived with the assumption of a quasi-steady state condition for the zwitterion concentration:

$$r = \frac{k_2 \cdot [\text{CO}_2] \cdot [\text{RNH}_2]}{1 + \sum \frac{k_{-1}}{k_i [\text{B}_i]}} \quad (5)$$

The second term in the denominator is $\ll 1$ and this results in simple second-order kinetics, as found experimentally for aqueous MEA solutions:

$$r = k_2 [\text{CO}_2] \cdot [\text{RNH}_2] \quad (6)$$

The reactions can then be summarized simply as:



When the concentration of MEA is much higher than that of the CO_2 in solution the MEA concentration can be considered as constant, leading to a pseudo-first order reaction with respect to the concentration of CO_2 . The temperature dependence of the rate constant k_2 was estimated (21) as:

$$k_2 = 4.4 \times 10^9 \exp\left(\frac{-5400}{T}\right) \quad (8)$$

This correlation was found to be valid across a wide range of temperatures (22) and is used to evaluate the experimental kinetic data in this work.

Rate of CO_2 Absorption

The overall mass transfer coefficient, K_G , for the CO_2 transfer across the gas and liquid films can be defined in terms of y_{CO_2} , the CO_2 molar fraction in the gas phase and $y_{\text{CO}_2}^*$, the hypothetical molar fraction equilibrium in equilibrium

with the bulk molar fraction in the liquid phase:

$$N_{\text{CO}_2} = K_G \cdot P \cdot (y_{\text{CO}_2} - y_{\text{CO}_2}^*) \quad (9)$$

$$\frac{1}{K_G} = \frac{1}{k_G} + \frac{H}{k_L \cdot \beta} \quad (10)$$

where k_G and k_L represent the mass transfer coefficients in the gas and liquid boundary films, respectively, and H and β stand for the Henry's constant and the enhancement factor, respectively. Assuming irreversible pseudo first order kinetics as above β can be expressed as;

$$\beta = \frac{\gamma}{\tanh \gamma} \quad (11)$$

where γ is defined as:

$$\gamma = \frac{\sqrt{k_2 \cdot [\text{RNH}_2] \cdot D_L}}{k_L} \quad (12)$$

An order of magnitude estimate of k_L can be determined from the correlation for pall rings (23):

$$k_L \cdot \left(\frac{\rho_L}{\mu_L \cdot g} \right)^{0.33} = 0.0051 \cdot \left(\frac{L}{a_t \cdot \mu_L} \right)^{0.67} \cdot \left(\frac{\mu_L}{\rho_L \cdot D_L} \right)^{-0.5} \cdot (a_t \cdot d_p)^{0.4} \quad (13)$$

here this correlation was chosen because the range of the operative conditions comprised the experimental conditions of this study. The properties used in estimation, viscosity, density, and surface tension, were 0.0047 Pa · s, 1019 kg · m⁻³ and 0.061 N · m⁻¹, respectively (24). The diffusion coefficient of carbon dioxide in the solution, D_L , was estimated using the data and N₂O analogy of Versteeg and van Swaaij (25) to be 1.44 × 10⁻⁹ m² · s⁻¹ and the diffusion coefficient in the gas, D_G , was obtained from the work of Marrero et al. (26) to be 1.44 × 10⁻⁵ m² · s⁻¹. Calculation of k_2 and k_L from Equations (8) and (13) respectively for the conditions used in this study (20 wt% MEA solution and liquid phase Reynolds numbers (=L/a_t · μ_L) of between 1.5 and 13) leads to values of γ greater than 50. In this case, Equation (11) can be approximated simply as $\beta = \gamma$. Eqs. (9) and (10) can then be expressed as:

$$N_{\text{CO}_2} = K_G p_{\text{CO}_2} \quad (14)$$

$$\frac{1}{K_G} = \frac{1}{K_G} + \frac{H}{\sqrt{k_2 \cdot [\text{RNH}_2] \cdot D_L}} \quad (15)$$

Under these conditions, the total mass transfer resistance is not affected by the liquid phase flowrate and the mass transfer resistance in the liquid phase is independent of k_L .

The following correlation (23) was used for estimation of the k_G value;

$$\left(\frac{k_G \cdot p_{BM}}{G_M}\right) \cdot Sc_G^{0.67} = 1.02 \times \left[\frac{d_{pe} \cdot G}{\mu_G \cdot (1 - \varepsilon)}\right]^{-0.35} \tag{16}$$

Figure 2 shows the contributions of local mass transfer resistances, $R_G(=1/k_G)$ and $R_L(=H/\sqrt{k_2} \cdot [RNH_2] \cdot D_L)$ (27), to the overall mass transfer resistance, $R_t(=1/K_G)$, the abscissa is the Reynolds number, Re_{G1} . The contribution can be affected only by two operational parameters, MEA concentration and G , if the value of k_2 is constant. Higher MEA concentration or lower Re_G shifts the total mass transfer resistance to the gas phase, while the liquid phase resistance becomes significant at low MEA concentrations and high gas flow rates. For $[MEA] = 3.0 \times 10^3 \text{ mol} \cdot \text{m}^{-3}$, the operative concentration of this study, the resistance in the gas phase is much larger than that in the liquid phase, i.e., the gas phase is controlling over the operations in this study.

EXPERIMENTAL PROCEDURE

Materials and Conditions

The materials used and experimental conditions are summarized in Table 1. MEA with 99% purity was purchased from Aldrich Co. Ltd. and an aqueous solution of MEA were used as absorbent, with the concentration fixed at $3.3 \times 10^3 \text{ mol} \cdot \text{m}^{-3}$ (20 wt%). Nitrogen and carbon dioxide of 99% purity were obtained from BOC Gases. Two kinds of packings

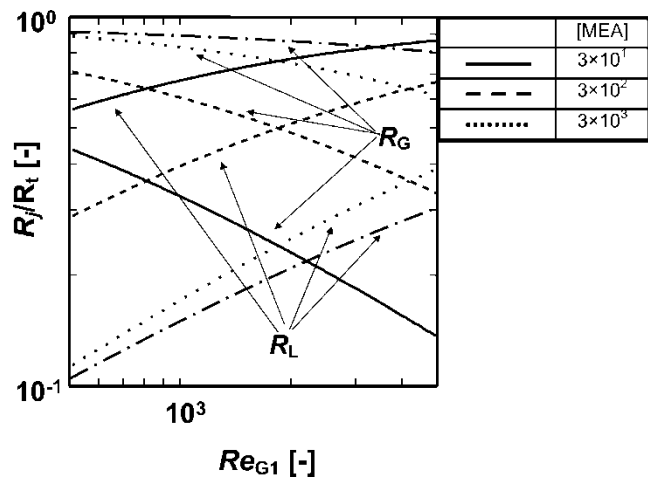


Figure 2. Contributions of local mass transfer resistances to overall mass transfer resistance (chained line is explained in Results and Discussion).

Table 1. Specification of column and experimental conditions for CO₂ absorption by MEA solution

Material	
Liquid phase	Aqueous solution of MEA ($3.33 \times 10^3 \text{ mol} \cdot \text{m}^3$)
Gas phase	Mixture of CO ₂ and N ₂
Specifications of column	
Column material	Glass
d_c [m]	0.076
Z [m]	1
Operational conditions of CO ₂ absorption	
$y_{\text{CO}_2, \text{B}}$ (feed gas) [–]	0.14
G [$\text{kg} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$]	$9.7 \times 10^{-2} - 8.1 \times 10^{-1}$
L [$\text{kg} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$]	1.1 – 3.9
T_a [K]	298

were used; stainless steel pall rings and SMRs. The nominal diameters of both packings are 13 mm and the total packing surface areas, a_t , of the SMRs and pall rings in the column are 420 m^{-1} and 360 m^{-1} , respectively obtained by actual estimation from the amounts of the packings in the column.

Experimental Procedure

Figure 3 shows a schematic diagram of the apparatus for continuous operation. The absorption experiments were performed in a column of $7.6 \times 10^{-2} \text{ m}$ internal diameter and 1.8 m total height, with a packing height of 1 m. N₂ and CO₂ were introduced to a gas mixer through flow meters to provide a gas mixture of 14 mol% CO₂, typical of flue gases from a coal fired power station. This mixture was fed to the base of the column through a distributor. The absorbent was freshly prepared before each run and similarly fed through a distributor to the top of the column. An hour was required for each run to attain steady state in the column. After reaching steady state samples of the exiting solution and gas streams were taken to be analyzed. Analysis was performed with a Shimadzu GC-8A gas chromatograph with TCD detector, to determine the CO₂, N₂ and MEA concentrations.

RESULTS AND DISCUSSION

Figure 4 shows the effects of packing species on gas holdup, ϕ_G as a function of the gas and solution phase Reynolds numbers, Re_{G2} and Re_{L2} . The gas

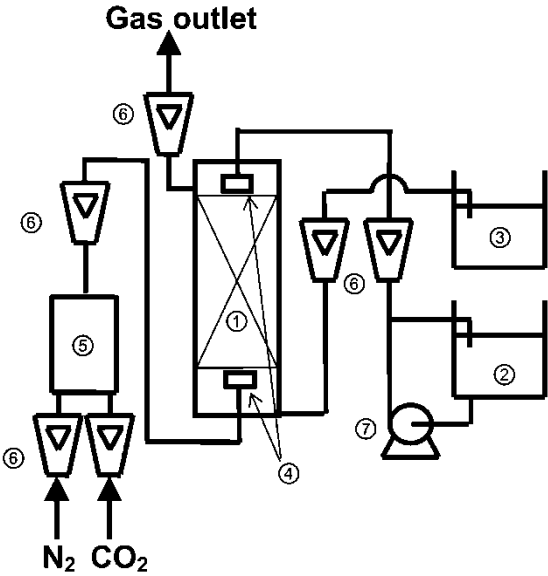


Figure 3. Schematic diagram of the packed column (1) packed column, (2) tank of absorbent solution, (3) tank for CO₂ loaded solution, (4) distributors, (5) gas mixer, (6) flow meter, (7) pump.

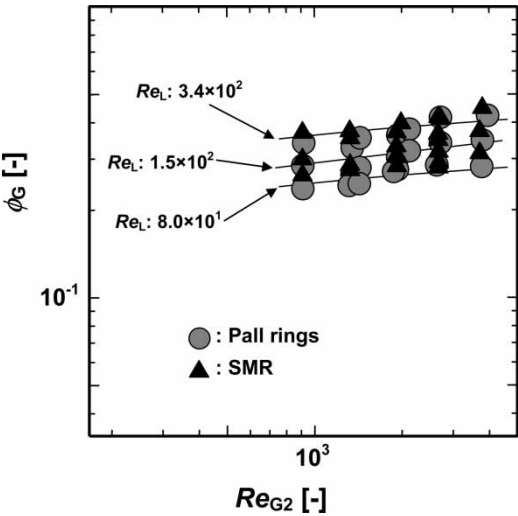


Figure 4. Holdup of gas phase for CO₂ absorption with MEA solution.

holdup increases with both an increase in G and an increase of L and the effects by G are smaller than L . The SMR packing gives approximately the same value of ϕ_G as the pall ring packing.

Figure 5 shows the effects of G and L on the frictional pressure gradient in the column, Δp , determined from the equation;

$$-\Delta p = -\frac{dp}{dz} + [\phi_G \cdot \rho_G + (1 - \phi_G) \cdot \rho_L] \cdot g_z \tag{17}$$

where the first term of right side is the apparent pressure drop along the packing part. The abscissa is the gas load factor, $F_G = u_G \cdot \sqrt{\rho_G}$. The SMR can reduce Δp by 15% to 20% relative to the pall ring and the value of Δp increases with an increase in G and L . This trend is almost identical with the results of PFMR packing for the measurement of oxygen stripping by Fei et al. (9). Though it is less significant to simply compare these results because of differences in the packing size and the employed system the values of Δp are larger in this study and the effects of both flow rates are smaller than that reported by Fei et al. (9). This might be caused by many factors; liquid properties, packing size, mass transfer behavior and any other factor. In particular, the smaller packing size of 13 mm relative to 16 mm packing in their study (9) should make its density higher in column, causing higher Δp , as seen in other articles (10).

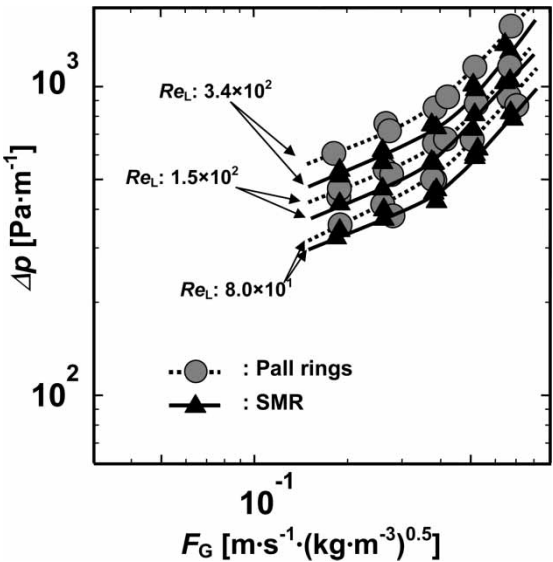


Figure 5. Effects of G and L on Δp .

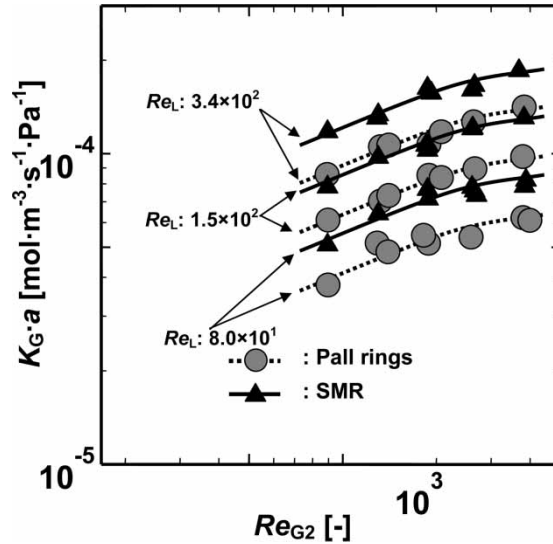


Figure 6. Effects of Re_G on $K_G \cdot a$.

Figure 6 shows the volumetric overall mass transfer coefficient in the gas phase, $K_G \cdot a$, calculated from;

$$G' \frac{dY_{CO_2}}{dz} = K_G \cdot a \cdot P \cdot (y_{CO_2} - y_{CO_2}^*) \quad (18)$$

The combination $K_G \cdot a$ increases substantially across all gas and liquid flow rates when the SMR is used in place of pall rings. The magnitudes of the $K_G \cdot a$ values are almost the same as the results of the previous research, measured with a 16 mm pall ring packed column (3) but $K_G \cdot a$ was approximately independent of gas flow rates in their study. This might be caused by the utilization of a higher MEA concentration solution ($7 \times 10^3 \text{ mol} \cdot \text{m}^{-3}$) increasing the liquid viscosity and shifting the controlling mass transfer resistance to the liquid phase.

The effective surface area, a , can be estimated from the correlation (28) for a range of packing systems and solvents:

$$\begin{aligned} \frac{a_w}{a_t} &= 1 - \exp \left[-1.45 \cdot \left(\frac{\sigma_C}{\sigma} \right)^{0.75} \cdot Re_{L1}^{0.1} \cdot Fr^{0.05} \cdot We^{0.2} \right] \\ &= 1 - \exp \left[-1.45 \cdot \left(\frac{\sigma_C}{\sigma} \right)^{0.75} \cdot \left(\frac{L}{a_t \cdot \mu_L} \right)^{0.1} \cdot \left(\frac{L \cdot a_t}{\rho_L^2 \cdot g} \right)^{-0.05} \right. \\ &\quad \left. \times \left(\frac{L^2}{\rho_L \cdot \sigma \cdot a_t} \right)^{0.2} \right] \end{aligned} \quad (19)$$

where the relationship of $a_w = a$ was ascertained to be effective when the reaction is the first order. The values of a are larger for SMR absorption than those for pall ring absorption due to the larger value of a_i of SMR; enhancing the specific surface area relative to the pall ring. With this estimation, k_G values for both packings were obtained, as shown in Fig. 6, and the trends of k_G values are identical because the packing shape has no influence on the k_G value. This result was also found in absorption studies with other systems, e.g. absorption of CH₃OH, NH₃ and acetone or other kinds of packings, ex. raschig rings, berl saddles and spheres (28–30) and it can be proved to be reasonable. The following correlation was obtained with estimated k_G values, shown as Fig. 7;

$$\left(\frac{k_G \cdot p_{BM}}{G_M}\right) \cdot Sc_G^{0.67} = 2.2 \times 10^{-1} \cdot \left[\frac{d_{pe} \cdot G}{\mu_G \cdot (1 - \varepsilon)}\right]^{-0.35} \tag{20}$$

The proportionality constant is lower than that of Eq. (16). The difference might result from the use of packing of size less than 15 mm, as absorption with smaller packing tends to give a smaller proportionality constant (28). Here the contributions of each local mass transfer resistance were estimated by using Eq. (15) to confirm the CO₂ absorption in this study and they are plotted in Fig. 2 by the chained line. The value of R_G is, as estimated above, much larger than R_L , and it was obvious that the mass transfer resistance in the gas phase governed the CO₂ absorption.

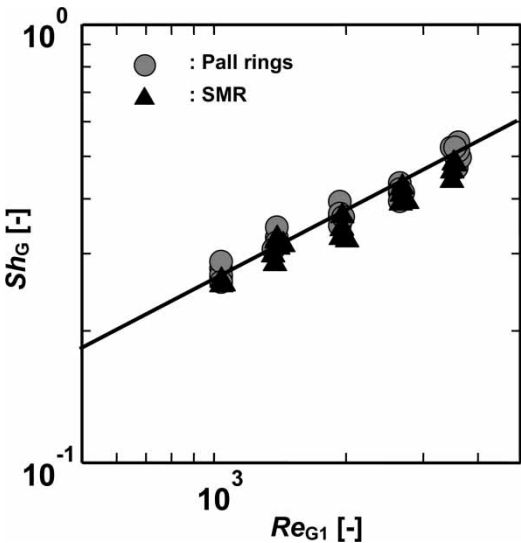


Figure 7. Correlation of Sh_G .

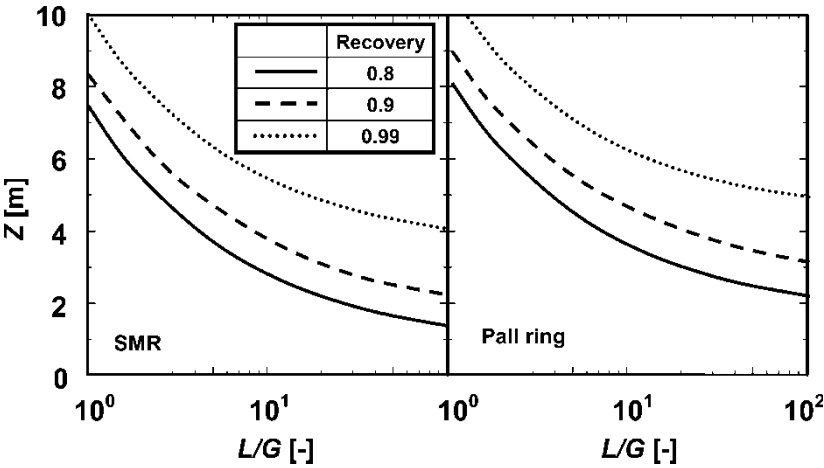


Figure 8. Required height of absorption column for CO₂ separation Feed gas composition of CO₂: 14 mol%, $T_a = 298$ K.

Process Concept and Simulation

The use of solvent absorption to capture carbon dioxide from power station flue gases is a challenging engineering exercise, due to the massive volume of gas requiring treatment and the low gas inlet pressure. Random packing is in some ways better suited to this application because of its lower price and lower pressure drop in the column. However, the specific surface area associated with such packing material is typically poor. The SMR discussed in this paper has the potential to provide a useful compromise by increasing the specific surface area. To quantify the potential benefits of this novel packing, the packing height was estimated for both pall rings and SMR over a range of column operating conditions. The required height of the absorption column, Z , was estimated by Eqs (18) to (20) and the calculation results are shown in Fig. 8. It is readily apparent that the SMR allows for a reduction in column height of around 20% relative to the use of pall rings.

CONCLUSIONS

The novel packing, the Super Mini Ring or SMR, offers higher absorption performance relative to pall rings due its smaller pressure drop and larger specific surface area. The case study presented shows the strong potential of SMR packing in that the required height of the packed column can be reduced by 20% relative to a pall ring column. Further work is required to determine

the behavior of this packing material under a broader range of operating conditions and to evaluate the hydrodynamics behavior, especially the gas holdup and the pressure drop induced by the packing.

NOMENCLATURE

a	effective surface area [m^{-1}]
a_t	total surface area of packing [m^{-1}]
a_w	wetted surface area of packing [m^{-1}]
D_G	diffusion coefficient of carbon dioxide in gas [$\text{m}^2 \cdot \text{s}^{-1}$]
D_L	diffusion coefficient of carbon dioxide in liquid [$\text{m}^2 \cdot \text{s}^{-1}$]
d_p	packing diameter [m]
d_c	column diameter [m]
d_{pe}	diameter of hypothetical sphere whose surface area is equivalent to the packing [m]
F_G	gas load factor [$\text{m} \cdot \text{s}^{-1} \cdot (\text{kg} \cdot \text{m}^{-3})^{0.5}$]
Fr	Froude number [—]
G	superficial flow rate of gas [$\text{kg} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$]
G'	superficial flow rate of inert gas [$\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$]
G_M	superficial flow rate of gas [$\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$]
H	Henry constant [$\text{Pa} \cdot \text{m}^3 \cdot \text{mol}^{-1}$]
K_G	overall mass transfer coefficient in gas phase [$\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$]
K_n	dissociation constant of reaction n [—]
k_i	forward reaction rate constant of reaction i [$\text{mol}^{-1} \cdot \text{m}^3 \cdot \text{s}^{-1}$]
k_{-i}	reverse reaction rate constant of reaction i [$\text{mol}^{-1} \cdot \text{m}^3 \cdot \text{s}^{-1}$]
k_G	mass transfer coefficient in gas phase [$\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$]
k_L	mass transfer coefficient in liquid phase [$\text{m} \cdot \text{s}^{-1}$]
k_2	reaction rate constant, defined by Eq. (8) [$\text{mol}^{-1} \cdot \text{m}^3 \cdot \text{s}^{-1}$]
L	superficial flow rate of liquid phase [$\text{kg} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$]
N_{CO_2}	flux of CO ₂ [$\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$]
P	total pressure [Pa]
p_{CO_2}	partial pressure of carbon dioxide [Pa]
p_{BM}	logarithmic mean partial pressure of inert gas along column [Pa]
$p_{\text{CO}_2}^*$	partial pressure of carbon dioxide [Pa]
p_{CO_2}	hypothetical partial pressure of carbon dioxide equilibrium with carbon dioxide concentration in solution [$\text{mol}^{-1} \cdot \text{m}^3 \cdot \text{s}^{-1}$]
Δp	frictional pressure difference [$\text{Pa} \cdot \text{m}^{-1}$]
R_j	mass transfer resistance of j ($=t, G$ or L) [$\text{mol}^{-1} \cdot \text{m}^2 \cdot \text{s} \cdot \text{Pa}$]
Re_G	Reynolds number of the gas phase ($Re_{G1} = d_{pe} \cdot G / \mu_G \cdot (1 - \varepsilon)$, $Re_{G2} = G \cdot D_c / \mu_G$) [—]
Re_L	Reynolds number of the liquid phase ($=L \cdot D_c / \mu_L$) [—]

r	reaction rate [$\text{mol} \cdot \text{m}^{-3} \cdot \text{s}^{-1}$]
Sc_j	Schmidt number of phase j [–]
Sh_j	Sherwood number of phase j [–]
t_j	time of j operation [s]
T_j	temperature of j operation [K]
u_j	superficial flow rate of phase j [$\text{m} \cdot \text{s}^{-1}$]
We_j	Webber number of phase j [–]
$y_{\text{CO}_2,\text{b}}$	molar fraction of carbon dioxide in feed gas [–]
Z	height of packing [m]
β	enhancement factor [–]
ε	void fraction in column [–]
ϕ_G	gas hold-up [–]
γ	Hatta number, defined as Eq. (12) [–]
σ	surface tension [$\text{N} \cdot \text{m}^{-1}$]
σ_c	critical surface tension [$\text{N} \cdot \text{m}^{-1}$]
μ_j	viscosity of phase j [$\text{Pa} \cdot \text{s}$]
ρ_j	density of phase j [$\text{kg} \cdot \text{m}^{-3}$]
$[\text{B}_i]$	concentration of base component i in solution [$\text{mol} \cdot \text{m}^{-3}$]
$[\text{CO}_2]$	concentration of carbon dioxide molecules in solution [$\text{mol} \cdot \text{m}^{-3}$]
$[\text{MEA}]$	concentration of monoethanolamine in solution [$\text{mol} \cdot \text{m}^{-3}$]
$[\text{RNH}_2]$	concentration of primary amine in solution [$\text{mol} \cdot \text{m}^{-3}$]

Subscripts

B	bottom of column
CO2	carbon dioxide
G	gas phase
i	component i or reaction i
j	phase j
L	liquid
N2	nitrogen
T	top of column
t	total
0	initial

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