A model on an entrained bed-bubbling bed process for CO_2 capture from flue gas

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Abstract−A simplified model has been developed to investigate effects of important operating parameters on performance of an entrained-bed absorber and bubbling-bed regenerator system collecting CO_2 from flue gas. The particle population balance was considered together with chemical reaction to determine the extent of conversion in both absorber and regenerator. The calculated CO_2 capture efficiency agreed with the measured value reasonably well. Effects of absorber parameters - temperature, gas velocity, static bed height, moisture content of feed gas on CO_2 capture efficiency - have been investigated in a laboratory scale process. The CO_2 capture efficiency decreased as temperature or gas velocity increased. However, it increased with static bed height or moisture concentration. The CO_2 capture efficiency was exponentially proportional to each parameter. Based on the absolute value of exponent of the parameter, the effect of gas velocity, static bed height, and moisture content was one-half, one-third, and one-fourth as strong as that of temperature, respectively.

Key words: CO_2 Capture, Model, Fluidized Bed, Entrained Bed, Sodium Carbonate

INTRODUCTION

Accumulation of CO_2 in the atmosphere is being recognized as one of important causes accelerating global warming. Many studies have found ways to remove CO_2 from flue gas massively with regenerable sorbents which are based on Na, K, and Ca [1-11]. The fluidized-bed CO_2 capture system consisting of a riser or a transport- or entrained-bed absorber and a bubbling-bed regenerator is used due to several potential advantages. The entrained bed can decrease the absorber diameter because of its high gas velocity. It is better to maintain a uniform temperature distribution and therefore it is easier to operate than the bubbling bed. A mathematical model can provide a tool for investigating the effects of various operating parameters on the reactor performance in advance. It is also good to save money and effort in systematic understanding of experimental result, design and operation. However, as yet there are no available reports on steady state analysis of the present process.

The purpose of this study was to develop a simplified model to investigate the effects of important operating parameters on the efficiency of an entrained bed - bubbling bed CO_2 capture process using a Na-based regenerable sorbent (Sorb-NH). A particle population balance was considered in both beds assuming negligible effect of chemical reaction. Reaction rates for absorption and regeneration were determined by kinetic rates measured with a thermogravimetric analyzer (TGA) and an experimental result obtained from a lab-scale continuous process of Korea Institute of Energy Research (KIER). Effects of several absorber parameters were investigated in the KIER's laboratory scale process.

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MODEL

Fig. 1 shows the schematic diagram of the process considered in this study, which uses an entrained-bed absorber and a bubbling-bed regenerator. Flue gas containing CO_2 is introduced to the absorber and fluidizes the bed of sorbent particles. Sodium-based sorbent particles were used to absorb CO_2 according to the following reaction:
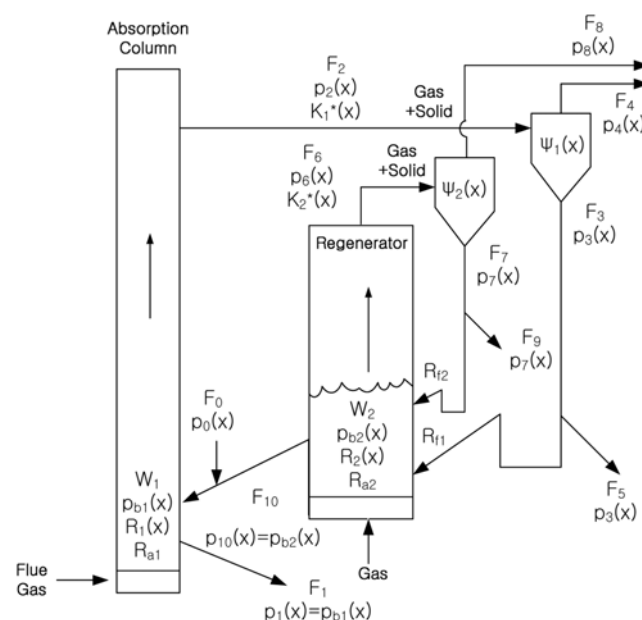

Fig. 1. Process flow diagram.

$$Na_2CO_3(s)+CO_2(g)+H_2O(g)=2NaHCO_3(s) \quad (1)$$

Reacted sorbent particles are carried out of the absorber, collected by a cyclone, and fed to the regenerator ($R_{f1}=1$, $F_1=F_5=0$). Steam is introduced to the regenerator and fluidizes the bed of sorbent particles. Sorbent particles containing CO_2 are regenerated according to the reverse reaction. Regenerated sorbent particles are returned to the absorber. The fractional collection efficiency of the cyclone ($\psi_i(x)$) is assumed as that of Lapple [12]. We assumed a well-mixed state of bed particles in both reactors ($p_1(x)=p_2(x)=p_{b1}(x)$, $p_{10}(x)=p_{b2}(x)$). The steady state particle population balance in the absorber ($i=1$) and regenerator ($i=2$) gives:

$$\frac{dp_{bi}(x)}{dx}+\sum_{k=1}^{2}\alpha_{ik}(x)p_{bk}(x)-\alpha_{i3}(x)=0 \quad (i=1,2) \quad (2)$$

$$\alpha_{i1}(x)=\delta_{1i}\left[\frac{F_1+K_1^*(x)}{W_1R_1(x)}+\frac{1}{R_1(x)}\frac{dR_1(x)}{dx}-\frac{3}{x}\right]-\frac{\delta_{2i}R_{f1}\psi_1(x)K_1^*(x)}{W_2R_2(x)} \quad (3a)$$

$$\alpha_{i2}(x)=-\frac{\delta_{1i}F_{10}}{W_1R_1(x)}$$
$$+\delta_{2i}\left[\frac{F_{10}+K_2^*(x)(1-R_{f2}\psi_2(x))}{W_2R_2(x)}+\frac{1}{R_2(x)}\frac{dR_2(x)}{dx}-\frac{3}{x}\right] \quad (3b)$$

$$\alpha_{i3}(x)=\frac{\delta_{1i}F_0p_0(x)+R_{ai}p_{ai}(x)}{W_iR_i(x)} \quad (3c)$$

B. C.: $p_{bi}(x)=0$ for $x=x_{max}$, constraint: $\int_0^{x_{max}}p_{bi}(x)dx=1$ (3d,e)

The δ_{ij} is the Kronecker delta. We used correlations of Choi et al. [13] for the particle entrainment rate $K_i^*(x)$ and the model of Merrick and Highley [14] for attrition rates R_{ai} and $R_i(x)$:

$$R_{ai}=K_a(u_i-u_{mfi})W_i, \quad R_i(x)=dx/dt=-K_a(u_i-u_{mfi})x/3 \quad (4a,b)$$

We assumed that fine particles formed by abrasion had diameter <5 μm, a uniform size distribution, and negligible attrition. The solid flow rate in the absorber is defined as

$$F_{10}=\beta(u_1-u_t)\rho_p\varepsilon_{s1}A_1, \quad (5)$$

The u_t is an average terminal velocity of particles, the ρ_p particle density, the ε_{s1} solid holdup and the A_1 bed area.

Reaction time of particles of a size was considered as their mean residence time in each reactor:

$$\tau_i(d_p)=\frac{W_{bi}\omega_{bi}(d_p)}{\sum_{j(out\text{-}flows)}S_{ij}\omega_{ij}(d_p)} \quad (6)$$

The average concentration of gas in each reactor was simply considered as an arithmetic mean value between inlet and outlet concentration:

$$\overline{C}_{ij}=\frac{C_{ij,0}+C_{ij,f}}{2} \quad (7)$$

Based on experimental data from TGA tests [1] and a continu-

ous process test of KIER (CO_2 capture efficiency: 0.0831; absorber condition: static bed height 0.5 m, gas velocity 3.0 m/s, temperature 50 °C), reaction rates for absorption and regeneration were determined:

$$\frac{dX}{dt}=\frac{0.337\times10^{-8}(1-X)}{d_p}e^{-E_1/RT_1}\overline{C_{CO_2}C_{H_2O}}, \quad E_1=-42.3 \text{ kJ/g mol} \quad (8)$$

B. C.: $X=X_{1i}(d_p)$ at t=0, $X=X_{1f}(d_p)$ at t=$\tau_1(d_p)$

$$\frac{d\lambda}{dt}=\frac{0.728\times10^{-2}(1-\lambda)}{d_p}e^{-E_2/RT_2}\frac{1}{\overline{C_{CO_2}C_{H_2O}}}, \quad E_2=50.4 \text{ kJ/g mol} \quad (9)$$

B. C.: $\lambda=0$ at t=0, $\lambda=\lambda_f(d_p)$ at t=$\tau_2(d_p)$; $X=X_{2i}(d_p)$ at t=0, $X=X_{2f}(d_p)=X_{1f}(d_p)(1-\lambda_f(d_p))$ at t=$\tau_2(d_p)$

The following relations between moles of CO_2 and moles of $NaHCO_3$ (formed and disappeared) must be satisfied in each reactor:

$$\Delta N_{1,NaHCO_3}=-2\Delta n_{1,CO_2}, \quad \Delta N_{2,NaHCO_3}=-2\Delta n_{2,CO_2} \quad (10)$$

By combining Eqs. (2) to (10), the present model can calculate the particle flow rate, particle size distribution, concentration of CO_2 in gas phase and $NaHCO_3$ in particles. The overall capture efficiency of CO_2 can be determined from the mole balance on CO_2.

SIMULATION CONDITIONS

The present model was applied to the KIER process (absorber: 0.025 m i.d., 6 m height; regenerator: 0.1 m i.d., 1.2 m height) [14]. Table 1 summarizes the size distribution of the fresh sorbent. The apparent particle density was 808 kg/m³. The following settings were held constant: pressure, 101.3 kPa; attrition coefficient of particle= 3×10^{-9} 1/mm; $F_1=0$, $R_{f2}=0$, $R_{f1}=1$ and $F_7=F_9$; temperature of the regenerator, 128 °C; gas velocity and static bed height of the regenerator, 0.02 m/s and 1.14 m, respectively; and fluidizing gas of the regenerator, pure N_2. Four absorber variables were tested in each range: static bed height in the absorber=0.3, **0.5**, 0.7 m; gas velocity in the absorber=**3.0**, 3.5, 4.0 m/s; temperature of the absorber= 40, **50**, 60, 80 °C; composition of feed gas to the absorber=N_2: balance, CO_2: 11.4%, H_2O: 5, **10**, 20, 30%. Other variables had the bold underlined values when a variable was tested.

RESULTS AND DISCUSSION

Table 2 shows CO_2 capture efficiencies measured in the KIER's process with variation of operating conditions [14]. The CO_2 capture efficiency was estimated by a mole balance on CO_2 in the absorber. Captured moles of CO_2 were determined as difference in mole flow rate of CO_2 between gas inlet and outlet of the absorber. It was checked well by the mole flow rate of CO_2 at the gas outlet of the regenerator. The CO_2 capture efficiency was a ratio of captured moles of CO_2 to feed moles of CO_2 for the absorber. There were very many variables involved in this process. In addition, the process had mechanical limitation to changing conditions of vari-

Table 1. Size distribution of fresh sorbent particles

Sieve size [μm]	−335+212	−212+150	−150+106	−106+75	−75+63	−63+53
Weight fraction	0.0122	0.1188	0.7036	0.0853	0.0772	0.0031

Table 2. Comparison between measured and calculated CO_2 capture efficiency ($u_2=0.02$ m/s)

Absorption column						Regenerator		CO_2 capture efficiency [-]	
h_{s1} [m]	F_{10} [kg/m²s]	u_1 [m/s]	T_1 [°C]	H_2O [%]	CO_2 [%]	h_{s2} [m]	T_2 [°C]	Measured	Calculated
0.341	29.4	2	54	10	11.4	1.14	128	0.067	0.082
2.78	29.4	2	52	10	11.2	0.5	87	0.073	0.115
1.31	22.1	2	45	10	11.4	1.09	89	0.145	0.136
1.67	28.0	2	49	15	11.4	1.04	78	0.164	0.121
1.53	25.6	2	60	20	11.4	0.91	104	0.172	0.168
1.31	42.6	2	51	10	15.4	0.79	83	0.107	0.084
3.19	42.6	1.75	43	10	9.2	0.7	121	0.282	0.232
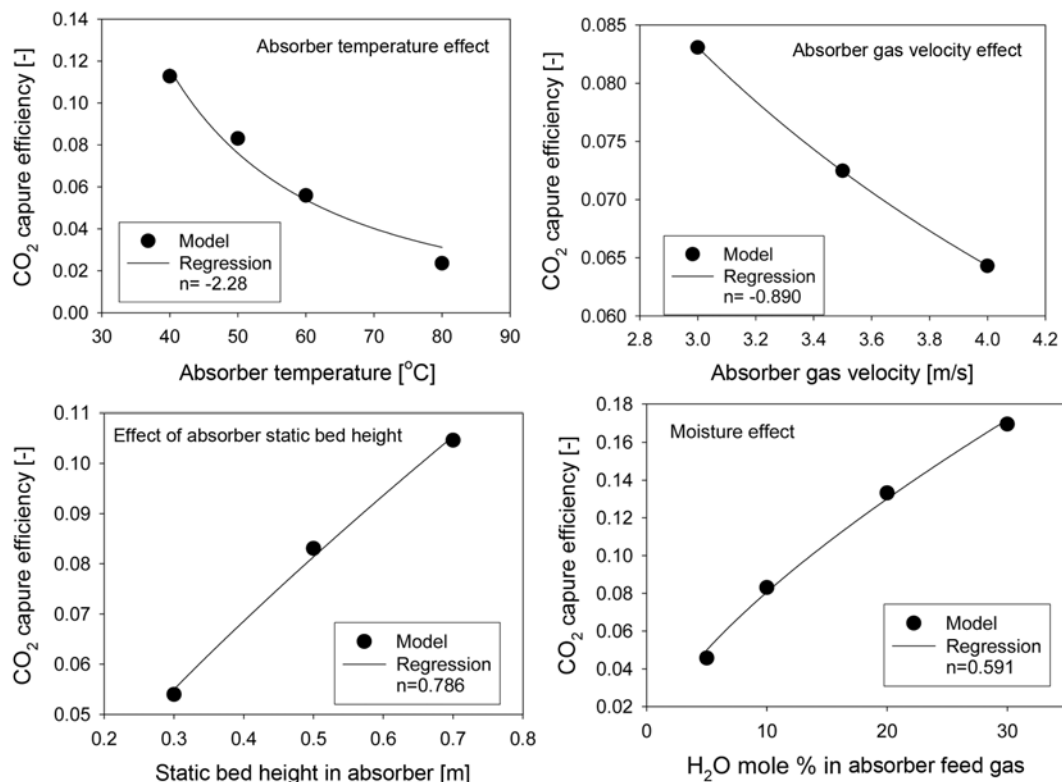
Fig. 2. Effects of absorber parameters on CO_2 capture efficiency.

ables. Therefore, the effect of a single variable could not be obtained. However, we could get reasonable agreement in comparison with the measured CO_2 capture efficiency with that calculated by the present model as shown in the table. Thus, the present model was used to investigate the single variable effect of the process. The single variable effect was examined in the condition that was employed by Choi et al. [15]. In their test range, the constant β of Eq. (5) was determined as 0.211 from the experimental data.

Fig. 2 shows the effects of absorber operating parameters on CO_2 capture efficiency predicted by the present model. The CO_2 capture efficiency decreased as temperature in the absorber increased. Because the absorption reaction is endothermic [1], the equilibrium moves in a reverse direction as temperature increases. Therefore, the extent of CO_2 capture decreases with an increase in temperature. The CO_2 capture efficiency is proportional to the absorber temperature with an exponent -2.28. The CO_2 capture efficiency decreased as gas velocity in the absorber increased. Retention time of CO_2 in the ab-

sorber decreases with an increase of gas velocity. Therefore, it caused a decrease of CO_2 capture. The CO_2 capture efficiency is proportional to the absorber gas velocity with an exponent -0.980. The CO_2 capture efficiency increased with an increase of static bed height in the absorber. It is because the absorption capacity increases with an increase of solid holdup in the absorber [17]. The CO_2 capture efficiency is proportional to the absorber's static bed height with an exponent 0.786. The CO_2 capture efficiency increased as the moisture content of flue gas increased, because the absorption reaction rate increases with moisture concentration [1]. Molar ratio of N_2 to CO_2 in the flue gas was maintained 0.786/0.114 constantly on calculations. The CO_2 capture efficiency is proportional to the moisture content of flue gas with an exponent 0.591.

CONCLUSIONS

We developed a simplified model to investigate the system behav-

ior and effects of important operating parameters for an entrained-bed absorption and bubbling-bed regeneration process which collects CO_2 from flue gas. The calculated capture efficiency agreed with the measured value reasonably well. Effects of four principal absorber parameters were tested in a laboratory scale process. The CO_2 capture efficiency decreased as temperature or gas velocity increased. However, it increased with an increase of solid holdup or moisture concentration. The CO_2 capture efficiency was exponentially proportional to each parameter. Based on the absolute value of the exponent of the parameter, the temperature appeared to have the strongest effect on the CO_2 capture efficiency. The effect of gas velocity, static bed height, and moisture content was about one-half, one-third, and one-fourth as strong as that of temperature, respectively.

ACKNOWLEDGEMENT

NOMENCLATURE

A_1 : bed area of absorber [m^2]

$C_{ij,o}$, $C_{ij,f}$, $\overline{C_{ij}}$: inlet, outlet, and average concentration of gaseous reactant j in reactor i [kg mol/m^3]

d_p : particle diameter [m]

E_i : activation energy of reaction i [kJ/g mol]

F_j : solid flow rate of stream j [kg/s]

h_{s1} : static bed height of absorber [m]

K_a : particle attrition rate constant [1/m]

$K_i^*(x)$: particle elutriation rate from bed i [kg/s]

n : exponent on independent variable [-]

$\Delta N_{i,NaHCO_3}$: total moles of $NaHCO_3$ in inflow of solids minus outflow of solids [kg mol/s]

$\Delta n_{i,CO_2}$: total moles of CO_2 in inflow of gas minus outflow of gas [kg mol/s]

$p_{ai}(x)$: probability density function of particles formed by attrition in bed i [1/m]

$p_{bi}(x)$: probability density function of particles in bed i [1/m]

$p_j(x)$: probability density function of particles in stream j [1/m]

$p_0(x)$: probability density function of fresh feed particles [1/m]

R : gas constant, 8.314 [kPa m^3/kg mol K]

R_{ai} : overall formation rate of fine particles by attrition in bed i [kg/s]

R_{fi} : recycle fraction of solid collected by cyclone [-]

$R_i(x)$: particle attrition rate in bed i [m/s]

S_{ij} : mass flow rate of total particle in outflow stream j from bed i [kg/s]

t : time [s]

T : temperature [K]

u_i, u_{mfi} : fluidizing and minimum fluidizing velocity in reactor i, respectively [m/s]

u_t : average terminal velocity of particles

W_i : weight of bed i [kg]

x, x_c, x_{max} : spherical particle diameter, cut diameter of cyclone and maximum x [m]

X_{ii}, X_{if} : conversion of Na_2CO_3 to $NaHCO_3$ for in- and out- flow of reactor i [-]

Greeks

α_{ik}, α_{i3} : functions defined as Eqs. (2a, b, c) [1/m, 1/m^2]

β : coefficient [-]

δ_{ij} : Kronecker delta [-]

ε_{s1} : solid holdup [-]

λ : conversion of regeneration reaction [-]

ρ_p : particle density [kg/m^3]

τ_i : mean particle residence time in reactor i [s]

$\psi_i(x)$: cyclone collection efficiency [-]

$\varpi_{bi}(x)$: mass fraction of particle in bed i [-]

$\varpi_{ij}(x)$: mass fraction of particle in outflow stream j from bed i [-]

Subscripts

ave, b : average and bed, respectively

i : free index, 1 for absorber and 2 for regenerator

j, k : indices

REFERENCES

1. C. K. Yi, S. W. Hong, S. H. Jo, J. E. Son and J. H. Choi, *Korean Chem. Eng. Res.*, **43**, 294 (2005).
2. C.-K. Yi, S.-H. Jo, Y. Seo, J.-B. Lee and C.-K. Ryu, *Int. J. Greenhouse Gas Control*, **1**, 31 (2007).
3. J. B. Lee, C. K. Ryu, J.-I. Baek, J. H. Lee, T. H. Eom and S. H. Kim, *Ind. Eng. Chem. Res.*, **47**, 4465 (2008).
4. C.-K. Yi, S.-H. Jo and Y. Seo, *J. Chem. Eng. Japan*, **41**, 691 (2008).
5. J. C. Abanades, M. Alonso, N. Rodriguez, B. Gonzalez, G. Grasa and R. Murillo, *Energy Procedia*, **1**, 1147 (2009).
6. M. Alonso, N. Rodriguez, G. Grasa and J. C. Abanades, *Chem. Eng. Sci.*, **64**, 883 (2009).
7. F. Fang, Z. Li and N. Cai, *Ind. Eng. Chem. Res.*, **48**, 11140 (2009).
8. K.-W. Park, Y. S. Park, Y. C. Park, S.-H. Jo and C.-K. Yi, *Korean Chem. Eng. Res.*, **47**, 349 (2009).
9. Y. C. Park, S.-H. Jo, K.-W. Park, Y. S. Park and C.-K. Yi, *Korean J. Chem. Eng.*, **26**, 874 (2009).
10. Y. Seo, S.-H. Jo, C. K. Ryu and C.-K. Yi, *J. Environ. Eng.*, **135**, 473 (2009).
11. J. Stroehle, A. Lasheras, A. Galloy and B. Epple, *Chem. Eng. Technol.*, **32**, 435 (2009).
12. C. E. Lapple, *Chem. Eng.*, **58**, 144 (1951).
13. J. H. Choi, I. Y. Chang, D. W. Shun, C. K. Yi, J. E. Son and S. D. Kim, *Ind. Eng. Chem. Res.*, **38**, 2491 (1999).
14. D. Merrick and J. Highley, *AIChE Symp. Ser.*, **70**, 366 (1974).
15. C. K. Yi, *Elemental technology development of a dry regenerable sorbent process for CO₂ capture from flue gas streams*, Korea Institute of Energy Research, Ministry of Science & Technology, DA1-210 (2005).
16. J. H. Choi, J. Y. Park, C. K. Yi, S. H. Jo, J. E. Son, C. K. Ryu and S. D. Kim, *Korean Chem. Eng. Res.*, **43**, 286 (2005).
17. D. Kunii and O. Levenspiel, *Fluidization Engineering*, 2ⁿᵈ Ed., Butterworth-Heinemann, Boston (1991).