REGENERATION OF CO₂-LOADED CARBONATE SOLUTION BY REDUCING PRESSURE

SUSUMU NII, YOSHIRO IWATA,
KATSUROKU TAKAHASHI AND HIROSHI TAKEUCHI
*Department of Chemical Engineering, Nagoya University,
Chikusa-ku, Nagoya 464-01.*

Key Words: Gas Absorption, Desorption, Carbon Dioxide, Carbonate, Alkanolamine

For the purpose of developing a CO₂ separation process for flue gas of low CO₂ partial pressure, a vacuum regeneration method for an absorbent with low CO₂-loading was experimentally investigated. Since additional energy is consumed for water vaporization accompanied by CO₂ desorption in the regeneration step, reducing the generation of water vapor becomes important for energy saving. A solution of potassium or sodium carbonate and bicarbonate mixture was used as a model solution of CO₂-loaded absorbent; a carbonate solution containing diethanolamine (DEA) was also examined. Rates of CO₂ desorption and water vaporization were obtained under the operating conditions of various pressures and temperatures. The rate ratio of water vaporization to CO₂ desorption became minimum at a pressure equal to the vapor pressure of water. The rate of CO₂ desorption at this pressure increased with temperature until 343 K and the increase was minimal beyond this temperature. The desorption rate was enhanced by the addition of DEA to the carbonate solution, and the rate reached a maximum at a high DEA concentration.

Introduction

The emission of carbon dioxide (CO₂) is considered one of the biggest cause of global warming. Reduction of CO₂ emitted as flue gases from a large-scale stationary source has become a worldwide problem. Removal of CO₂ from high pressure process gas has been achieved in industry by gas absorption processes employing alkanolamines⁷⁾ or carbonates as absorbents^{2, 3, 7)}. However, it is difficult to apply these processes to flue gas decarbonization, for the partial pressure of CO₂ is low and the amount of gas is enormously large. Thus, a large amount of absorbent must be used to treat such a quantity of gas. High-level regeneration of the absorbent is indispensable for treating a gas of such a low partial pressure of CO₂. Since the regeneration step includes heating of the absorbent, the energy requirement will significantly increase when treating a large volume of absorbent with a low CO₂-loading. Therefore, the reduction of heating energy becomes a determining factor for realizing a wet decarbonization process.

From the viewpoint of energy saving in regeneration of the absorbent, a carbonate solution may be preferable to an alkanolamine solution. Although a carbonate solution is not suitable for deep CO₂ removal due to its small absorption rate and low absorption capacity compared to an amine solution, the energy requirement for CO₂ removal in the carbonate process is about a half of that of the conventional monoethanolamine process¹⁾. The rate of CO₂ absorption and desorption with carbonate solution can

be enhanced by the addition of amines^{1, 8)}. Therefore, the present study is focused on suggesting an effective regeneration method for the CO₂-loaded carbonate solution.

The difficulty in regenerating a carbonate solution of low CO₂-loading can be clearly noted from the vapor-liquid equilibrium reported by Tosh *et al*¹¹⁾. Even if the vapor phase is assumed to be in equilibrium with the liquid phase, the amount of water vapor accompanied with CO₂ desorption varies drastically with the CO₂-loading ratio, α , as shown in **Fig. 1**. A definition of α is given in the figure. When α is high, it corresponds to a high pressure process. Here, the water vapor pressure is comparable to that of CO₂. On the other hand, when α is low, i. e., in the case of absorption from a flue gas, the water vapor pressure is about ten times larger than that of CO₂. When taking into account the mass-transfer resistance, it is expected that the difference in the amount of water vaporization accompanied with CO₂ desorption becomes larger. It is suggested that a lot of heat is used to evaporate the water for regeneration of an absorbent of low α . By adopting a vacuum regeneration method, the operating temperature can be lowered where the partial pressure ratio of water to CO₂ is small. Therefore, an operation repressing water vapor generation may be possible, which leads to energy saving.

There have been a few studies on desorption from carbonate solutions^{1, 4, 8, 9)}. These studies dealt with the kinetics of the CO₂ desorption reaction^{1, 4)} and the expression of the desorption rate^{8, 9)}. The water vapor accompanied with the desorption of CO₂ was not discussed. The purpose of the present study is to suggest an optimum operating condition for vacuum regeneration of carbonate solution

* Received August 1, 1994. Correspondence concerning this article should be addressed to K. Takahashi.

Fig. 1 Effect of temperature for various CO₂-loading ratios on the ratio of partial pressure of H₂O to that of CO₂ in equilibrium

Fig. 2 Schematic diagram of experimental apparatus

in terms of the ratio of rates of CO₂ desorption and water vaporization. Furthermore, enhancement of the desorption rate by addition of diethanolamine to the carbonate solution is also discussed.

1. Experimental

As a model solution of CO₂-loaded absorbent, an aqueous solution was prepared by mixing potassium carbonate and potassium bicarbonate at various fractions. The CO₂-loading ratio was varied with the ratio of bicarbonate salt to carbonate salt. In some experiments, sodium salts were used instead of potassium salts. In the amine system, diethanolamine (DEA) was mixed with a carbonate-bicarbonate salt solution, because Mahajani and Danckwerts⁸⁾ reported that the promotion factor of DEA for CO₂ desorption was larger than those of other amines.

The experimental set-up is shown in Fig. 2. Experiments of CO₂ desorption were performed with a cylindrical glass cell (I.D. 55mm) connected to a vacuum air pump with a tube and a stop valve. The cell was soaked in a constant temperature water bath whose temperature ranged from 333 K to 358 K. 50 × 10⁻⁶ m³ of the model absorbent solution was poured into the cell and stirred by

Fig. 3 CO₂ desorption rate from bicarbonate salt solution

a magnetic stirrer while maintaining a flat gas-liquid interface. After ten minutes of stirring, the stop valve was opened and the cell was evacuated using the vacuum pump; the pressure was adjusted with the air leak valve. The desorption experiment was carried out at a constant temperature and pressure for a given time. The cell and the solution were weighed together before and after desorption, and the amount of vaporized water was determined from the difference of these weights. The solution was titrated with an aqueous solution of HCl by using an automatic titrator (COMTITE-101 Hiranuma Co. Ltd.).

The concentrations of carbonate ion and bicarbonate ion were determined from two end points in a titration curve. For the absorbent solution containing amine, a titration curve had three end points. However, the first and the second end points were ambiguous, and it was difficult to determine the concentrations of HCO₃⁻ and CO₃²⁻. When Ba(OH)₂ was added to the absorbent solution, the titration curve had two end points. By using these two end points together with the third end point in the curve of direct titration, the concentrations of HCO₃⁻ and CO₃²⁻ were determined. The CO₂ desorption rate was calculated in terms of the change in concentration of these ions.

2. Results and Discussion

2.1 Desorption rate of CO₂

When CO₂ is absorbed into a carbonate solution, the following equilibrium reaction proceeds to the right to generate bicarbonate ion.

Regeneration of the absorbent is to convert the bicarbonate ion to carbonate ion. Conditions of high temperature and reduced pressure are favorable to shift the equilibrium. To evaluate the degree of regeneration, the CO₂-loading ratio, α was defined as

Fig. 4 Effect of pressure on CO₂ desorption rate

$$\alpha = \frac{[\text{HCO}_3^-]}{[\text{HCO}_3^-] + 2[\text{CO}_3^{2-}]} \quad (1)$$

The value of α increases with the ratio of bicarbonate to carbonate, which varies in the range of 0 to 1. In the case of pure carbonate solution, $\alpha = 0$, and in the case of pure bicarbonate solution, $\alpha = 1$, i.e., α decreases with the regeneration degree. The desorption rates of CO₂ from the bicarbonate solution, J_{CO_2} are shown in Fig. 3. There was no difference between the desorption rates from sodium salt and potassium salt solutions. The value of J_{CO_2} increased in proportion to the power of 1.4 of salt concentration as shown by a solid line in Fig. 3. The salt concentration refers to the concentration of cation, $C = 2 [\text{K}_2\text{CO}_3] + [\text{KHCO}_3]$, for potassium salt. In general, the absorption rate of CO₂ decreases with the salt concentration because of a decrease in CO₂ solubility. The effect of CO₂ solubility on the desorption rate may be inverse to that on the absorption rate. By using Henry's constant for CO₂-water, H_w , and CO₂-salt solution, H^s , the corrected desorption rate, $J_{\text{CO}_2} (H_w/H)$ is also plotted in Fig. 3 and shown in closed symbols. These corrected values are proportional to the salt concentration as shown by the dashed line. Owing to the high solubility of potassium bicarbonate, a solution of high concentration can be prepared by using the potassium salt. Hereafter, experiments were carried out with potassium salt.

Figure 4 shows effects of pressure and temperature on CO₂ desorption rate for the desorption from the solution of CO₂-loading ratio $\alpha = 0.5$. J_{CO_2} increases with decreasing pressure, P , and the change in J_{CO_2} is large below the vapor pressure of water which is indicated by an arrow in the figure. Since the interfacial area increased because of boiling of the solution at low pressure, the apparent J_{CO_2} might increase rapidly. The desorption rate also increases largely with the temperature as shown in Fig. 4. At a pressure equal to the vapor pressure of water, the CO₂ desorption rate at 343 K is equal to that at 353 K, and high temperature is not necessarily favorable for CO₂ desorption.

2.2 Calculation of desorption rate

The overall reaction for CO₂ desorption from carbonate and bicarbonate mixture solution is expressed as the reaction (r-1). The reaction consists of two steps. When

there is no catalyst in the solution, these are⁴⁾

Because the reaction (r-3) is much faster than the reaction (r-2), the rate determining step is (r-2). Pohorecki and Kucharski⁹⁾ expressed the pseudo first-order rate constant k_1 for the reaction (r-2) as

$$k_1 = K_R \frac{[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \quad (2)$$

$$\text{where } K_R = k_{\text{OH}^-} \frac{K_w}{K_2} \quad (3)$$

K_w is the water dissociation constant defined as $K_w = [\text{H}^+][\text{OH}^-]$ and K_2 the equilibrium constant defined as $[\text{H}^+][\text{CO}_3^{2-}]/[\text{HCO}_3^-]$. They also derived a correlation for the kinetic coefficient, K_R , in the temperature range 333 – 473 K and ionic strength 2–8 kmol/m³ as follows.

$$\ln K_R = 27.821 - 8514/T + 0.5456I - 0.02760I^2 \quad (4)$$

The rate of desorption under a first-order reaction can be given as⁴⁾

$$N_A = (C_{A,e} - C_{A,i}) (D_A k_1 + k_c^2)^{0.5} \quad (5)$$

where $C_{A,i}$ is CO₂ concentration at the interface, $C_{A,e}$ the equilibrium concentration of CO₂ in the bulk of liquid, D_A diffusivity of CO₂ in the liquid and k_c the liquid film mass-transfer coefficient. Because the term of k_c^2 is much smaller than the reaction term, the effect of physical transfer could be neglected¹²⁾. Furthermore, by assuming that $C_{A,i}$ is negligible under vacuum conditions, Eq. (5) is reduced to

$$N_A = C_{A,e} (D_A k_1)^{0.5} \quad (6)$$

$C_{A,e}$ is calculated from the equilibrium in the liquid.

$$C_{A,e} = \frac{K_2 [\text{HCO}_3^-]^2}{K_1 [\text{CO}_3^{2-}]} \quad (7)$$

where K_1 is the equilibrium constant defined as $[\text{H}^+][\text{HCO}_3^-]/[\text{CO}_2]$. The values of K_1 and K_2 are obtained from the correlation given by Kent and Eisenberg⁶⁾.

If the interfacial area between the gas and liquid did not change during the operation, i.e., as long as the flat interface was kept, the desorption rate could be calculated as follows. Concentrations of HCO_3^- and CO_3^{2-} were determined from the total salt concentration and the definition of α . The kinetic coefficient K_R was given by the correlation of Eq. (4), then the rate constant k_1 was calculated by Eq. (2). By using CO₂ diffusivity, the CO₂ desorption rate was obtained from Eq. (6).

When boiling occurs, the interfacial area is increased by bubble formation. Thus, Pohorecki and Kucharski suggested a factor for correcting the effect by the following equation⁹⁾.

Fig. 5 Effect of CO₂-loading ratio on CO₂ desorption rate

$$S = \frac{a^*}{a} = \frac{p_{\text{CO}_2}^* + p_{\text{H}_2\text{O}}}{P} \quad (8)$$

where a^* is the interfacial area for the case of boiling, $p_{\text{CO}_2}^*$ the equilibrium partial pressure of CO₂ given by Henry's law and P the operating pressure. The water vapor pressure for salt solution was calculated from the depression of the vapor pressure by the presence of the salt. Boiling leads to an increase in the value of S beyond 1.0. The desorption rate is thus obtained by multiplying the correction factor to the flux calculated from Eq. (6).

Figure 5 shows the effect of CO₂-loading ratio on CO₂ desorption rate and a comparison between calculated values and observed ones. Observed values are obtained at a pressure equal to the water vapor pressure at each temperature. The desorption rate increases exponentially with increasing CO₂-loading ratio of the solution. There is reasonable agreement between observed values and calculated lines at 333 K and 353 K. However, the observed values at 343 K were larger than the calculated ones.

2.3 Vaporization rate of water

The decrease in total pressure led to an increase in the vaporization rate of water as well as CO₂ desorption rate. Figure 6 shows the water vaporization rate at various operating pressures. Although the behavior of the water vaporization rate versus pressure is similar to that of the CO₂ desorption rate shown in Fig. 4, the water vaporization rate is over a hundred times larger than the desorption rate of CO₂. This means that a lot of additional heat was used for water vaporization during CO₂ desorption. Thus, the favorable operating condition for energy saving operation has to be determined.

The ratio of water vaporization rate to CO₂ desorption rate is plotted against the operating pressure in Fig. 7. The plot shows a minimum at a pressure just equal to the water vapor pressure. This means that the evaporated water accompanying the desorbed CO₂, i.e., the energy for water vaporization, is lowest at the water vapor pressure. Lowering of the temperature leads to a decrease in the ratio due to a decrease in the water vaporization rate. Therefore,

Fig. 6 Effect of pressure on water vaporization rate

Fig. 7 Ratio of water vaporization rate to CO₂ desorption rate

the favorable operating condition is considered to be a pressure equal to the water vapor pressure.

2.4 Effect of temperature on CO₂ desorption rate

The effect of temperature on the CO₂ desorption rate from carbonate-bicarbonate solution at a pressure equal to the water vapor pressure is shown by open symbols in Fig. 8. The dashed line represents calculated values which are obtained from Eq. (6) and Eq. (8). The observed desorption rate of CO₂ increases with increasing temperature until 343 K. Beyond this temperature, the rate increases only slightly. There is no remarkable difference between the rates at 343 K and 353 K. Therefore, operation at 343 K realizes both a high desorption rate of CO₂ as well as low vaporization of water as shown in Fig. 7.

Mahajani and Danckwerts studied CO₂ desorption from aqueous carbonate buffer solutions by a gas sweeping method at 373 K and ambient pressure⁸⁾. They reported a CO₂ desorption flux of 1.76×10^{-6} kmol/(m².s) for $C = 5.6$ kmol/m³ and $\alpha = 0.45$. Our experimental CO₂ desorption rate was 3.9×10^{-7} kmol/(m².s) for a solution of $C = 3.0$ kmol/m³ at 343 K. This value was converted to the value corresponding to $C = 5.6$ kmol/m³ by using the relation between the CO₂ desorption rate and salt concentration that was presented in Fig. 3. The converted value was 2.06×10^{-6} kmol/(m².s); it is comparable to the value for the gas sweeping method at 373 K. It suggests that the vacuum method at lower temperature gives about the same CO₂ desorption rate as in the gas sweeping method.

Fig. 8 Effect of temperature and DEA addition on CO₂ desorption rate

Thus, the heating energy can be reduced by adopting the vacuum method. However, to evaluate the total energy requirement for CO₂ desorption, the energy for pressure reduction must be taking into consideration.

2.5 Effect of DEA addition on desorption rate

Figure 8 also shows the effect of DEA addition to the carbonate-bicarbonate solution on the CO₂ desorption rate. The solid line represents calculated values for carbonate solution containing DEA. The value is given by multiplying the enhancement factor to the value calculated for the case without DEA. Mahajani and Danckwerts⁸⁾ suggested that the enhancement factor, E , is given by

$$E = \frac{\frac{[\text{HCO}_3^-]^2}{[\text{CO}_3^{2-}]} \sqrt{B_0 \frac{[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} + B_1 (\text{AmH})}}{\frac{[\text{HCO}_3^-]_0^2}{[\text{CO}_3^{2-}]_0} \sqrt{B_0 \frac{[\text{CO}_3^{2-}]_0}{[\text{HCO}_3^-]_0}}} \quad (9)$$

where B_0 and B_1 are defined as follows,

$$B_0 = 10^6 D_A k_{\text{OH}^-} K_W K_2 / K_1^2 \quad (10)$$

$$B_1 = 10^6 D_A k_{\text{am}} K_W (K_2 / K_1)^2 \quad (11)$$

where k_{am} is the forward reaction rate constant for the following reaction between CO₂ and free amine

They gave a value of $k_{\text{am}} = 7 \times 10^5 \text{ m}^3/(\text{kmol}\cdot\text{s})$ for DEA. The value of k_{OH^-} was estimated from the value of $k_{\text{OH}^-} K_W / K_2 = 1.9 \times 10^4 \text{ s}^{-1}$ at 373 K reported by Savage *et al.*¹⁰⁾ The values of D_A , K_1 and K_2 are listed in Table 1 as well as the calculated enhancement factor. The observed values of promoted J_{CO_2} are in reasonable agreement with the calculated line.

Figure 9 shows the effect of DEA concentration in the carbonate solution on the CO₂ desorption rate. The solid line denotes the calculated values based on Eq. (9). The CO₂ desorption rate, shown by open symbols, goes through a maximum with increasing DEA concentration, wherein CO₂-loading ratios of the solution defined by Eq. (1) are used. The maximum appears because of the decrease in

Fig. 9 Effect of DEA concentration on CO₂ desorption rate

Table 1 Enhancement factor and constants

temp.[K]	D_A^* [m ² /s]	K_1^{**} [kmol/m ³]	K_2^{**} [kmol/m ³]	E [-]
333	1.9×10^{-9}	5.58×10^{-7}	7.21×10^{-11}	3.3
343	2.1×10^{-9}	5.40×10^{-7}	7.51×10^{-11}	2.6
353	2.2×10^{-9}	5.11×10^{-7}	7.68×10^{-11}	1.8

* from reference 10, ** from reference 6

essential CO₂-loading ratio of the solution in the range of high DEA concentration. That is, the addition of DEA leads to an increase in the CO₂ absorbing capacity of the solution; the effect becomes remarkable at high DEA concentration. Therefore, the definition of the CO₂-loading ratio of the alkanolamine-containing carbonate solution is corrected as the following equation.

$$\alpha' = \frac{[\text{HCO}_3^-]}{[\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{AmH}]} \quad (12)$$

The value of α' is smaller than α , and varies with the DEA concentration. To compare the J_{CO_2} between DEA-free solution and DEA-containing solution at equal CO₂-loading ratios, observed values of the CO₂ flux at α' were converted to the value of $\alpha' = 0.5$ using the relation between J_{CO_2} and α for carbonate solution obtained in Fig. 5. The closed symbols in Fig. 9 denote the corrected values of CO₂ desorption rate. In the range of low concentration of DEA, the tendency of the corrected desorption rate is in accordance with the calculated line. Although the corrected rate reached a maximum at a high DEA concentration, the calculated value continues increasing. The addition of DEA up to 0.24 kmol/m³ may be effective for enhancement of CO₂ desorption. In addition, the water vaporization rate of DEA-containing solution decreased slightly in the presence of DEA and there was only a weak dependence of the rate on DEA concentration. This implies the addition of DEA until the limiting concentration is effective for the enhancement of CO₂ desorption rate.

Conclusion

The desorption rates of CO₂ and H₂O from CO₂-loaded carbonate solution and DEA-containing solution were measured under reduced pressure and at various

temperatures. Operation at a pressure equal to the water vapor pressure minimized the amount of water vapor accompanying CO₂ generation. The CO₂ desorption rate increased with rising temperature until 343 K, and a further rise in temperature did not cause an increase in the desorption rate, but an increase in the water vaporization rate. The desorption rate of CO₂ increased exponentially with the CO₂-loading ratio of the absorbent. The addition of DEA to the carbonate solution enhanced the CO₂ desorption rate, and the rate reached a maximum at a high DEA concentration.

Nomenclature

a	=	interfacial area	[m ²]
a^*	=	interfacial area including effect of bubbling	[m ²]
C	=	concentration	[kmol/m ³]
$C_{A,e}$	=	Equilibrium concentration of CO ₂ in the liquid bulk	[kmol/m ³]
$C_{A,i}$	=	CO ₂ concentration at the interface	[kmol/m ³]
D_A	=	Diffusivity of CO ₂ in the liquid	[m ² /s]
H	=	Henry's constant	[kPa·m ³ /kmol]
I	=	ionic strength	[kmol/m ³]
J	=	flux	[kmol/(m ² ·s)]
K_R	=	kinetic coefficient given by Eq. (3)	[s ⁻¹]
K_w	=	water dissociation constant	[kmol ² /m ⁶]
K_1	=	equilibrium constant defined as $[H^+][HCO_3^-]/[CO_2]$	[kmol/m ³]
K_2	=	equilibrium constant defined as $[H^+][CO_3^{2-}]/[HCO_3^-]$	[kmol/m ³]
k_c	=	mass-transfer coefficient in the liquid film	[m/s]
k_{OH^-}	=	rate constant for reaction (r-2)	[m ³ /(kmol·s)]

k_1	=	pseudo first-order rate constant	[s ⁻¹]
P	=	operating pressure	[kPa]
$P_{CO_2}^*$	=	equilibrium partial pressure of CO ₂	[kPa]
P_{H_2O}	=	water vapor pressure	[kPa]
T	=	temperature	[K]
S	=	correction factor for bubble occurring	[-]

α	=	CO ₂ -loading ratio defined by Eq. (1)	[-]
α'	=	CO ₂ -loading ratio defined by Eq. (12)	[-]

< Subscript >

0	=	initial condition
---	---	-------------------

Literature Cited

- 1) Astarita, G., D.W. Savage and A. Bishio: "Gas Treating with Chemical Solvents", John Wiley & Sons (1983)
- 2) Bartoo, R.K. and U.C. Corp: *Chem. Eng. Prog.*, Oct., 35-39 (1984)
- 3) Benson, H.E., J.H. Field and W.P. Hanes: *Chem. Eng. Prog.*, **52**, 433-438 (1956)
- 4) Danckwerts, P.V.: "Gas Liquid Reactions", McGraw-Hill (1967)
- 5) Kagakukogaku Kyokai: "Kagakukogaku Benran", p58, Maruzen (1988)
- 6) Kent, R.L. and B. Eisenberg: *Hydrocarbon Processing*, Feb., 87-90 (1976)
- 7) Kohl, A.L. and F.C. Riesenfeld: "Gas Purification", 4th ed., Gulf Publishing Co., Houston, TX (1985)
- 8) Mahajani, V.V. and P.V. Dankwerts: *Chem. Eng. Sci.*, **38**, 321-327 (1983)
- 9) Pohorecki, R. and E. Kucharski: *Chem. Eng. J.*, **46**, 1-7 (1991)
- 10) Savage, D.W., G. Astarita and S. Joshi: *Chem. Eng. Sci.*, **35**, 1513-1522 (1980)
- 11) Tosh, J.S., J.H. Field, H.E. Benson and W.P. Haynes: Rept. No.5484, U.S. Bur. Mines, 1-23 (1959)
- 12) Tseng, P.C., W.S. Ho and D.W. Savage: *AIChE J.*, **34**, 922-931 (1988)