Desorption Of Carbon Dioxide From Promoted Hot Potassium Carbonate In An Industrial Stripper Using Penetration Theory

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ABSTRACT

A mathematical model was used for simulation of CO_2 desorption from promoted hot potassium carbonate solution. The combined effects of chemical reaction and mass transfer were conveniently and adequately treated within the framework of the penetration-surface renewal theory. The vapor-liquid equilibrium data for the un-promoted carbonate-CO_2 was employed for developing the model which seems to be adequate at low concentration of amine for the system. The operating data for carbon dioxide desorption from DEA-hot potassium carbonate solution in an industrial stripper has been compared to model predictions. The process model was used to predict profiles of different dependent parameters in a commercial desorption unit. The effects of the promoter concentration, the promoter type and the inlet temperature of rich solution on the performance of an industrial regeneration unit have also been examined. It was found that the inlet liquid temperature impact upon both the mass transfer and the reboiler steam consumption rate. © 2007 Trade Science Inc. - INDIA

INTRODUCTION

For economic reasons it is almost necessary to regenerate the spent solution from a carbon dioxide absorption column so that the absorbent can be re-cycled. The design of columns for stripping solutions which contain physically dissolved gases is comparatively simple. However, complications arise when chemical reactions are involved. The relevant information on this subject in the literature is very scarce, although the investment for the desorption columns with or without chemical reactions is considerably greater than that for the absorption columns.

The regeneration often uses steam or heated inert gas as stripping agents. As a result, an accurate

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design based on proper chemical and mass transfer data could lead to significant energy savings. The gas to be purified is generally under pressure; therefore absorber operates under high pressure, while stripper operates at about atmospheric pressure. Essentially, the process depends on the pressure difference between the absorber and stripper and a substantial difference in temperature is not necessary. In stripping columns, steam (either live or from a reboiler at the bottom of stripper) or hot air are used to strip the carbon dioxide from absorbent. The quantity of stripping vapor required depends upon the solution purity needed to produce the required product gas, the stripping column height and the nature of the solution.

The applicability of potassium carbonate to CO_2 removal has been known for many years. A German patent granted as early as 1908, described a process for absorbing CO_2 in a hot solution of potassium carbonate and then stripping the solution by pressure reduction without additional heating[1]. In 1924, Williamson and Mathews studied the rate of absorption of CO_2 in potassium carbonate solution and found that increasing temperature greatly increased the rate of absorption[2]. The hot carbonated process was developed by Benson et al.[3, 4]. Benson indicated that because the CO_2 concentration in solution decreases rapidly with decreased partial pressure of CO_3 over it, solution regeneration can be carried out most effectively at a very low pressure[5]. The high temperature increases the solubility of potassium bicarbonate thus permitting operation with a highly concentrated solution that increases the carrying capacity for acid gases per gallon of solution. In addition steam required to heat the solution for stripping temperature is less. The basic hot carbonated process has since undergone several improvements[6, 7], that some of these aimed primarily at greater heat economy[8, 9,10].

The concept of adding amine to carbonate systems for enhancement of CO_2 absorption has been known for a long time[11-16]. However, there is no information available in the literature regarding the desorption of carbon dioxide from potassium carbonate in an industrial regeneration column. Therefore, we decided to study the phenomenon of desquire research including the effect of parameters such as promoter type and concentration which are

discussed in the present work. Other areas include the effect of amine additives on the equilibrium and the influence of reactants and products diffusion in the mass transfer boundary layer on the enhancement factor.

In our previous work we have investigated the absorption of carbon dioxide into potassium carbonate in an absorption column[17], while in this work desorption of carbon dioxide from potassium carbonate in a stripper column is investigated. A general model for the mass transfer/reaction processes in carbon dioxide stripper using promoted hot potassium carbonate has been developed and the combined effects of mass transfer and chemical reaction was treated by the surface-renewal penetration theory. In addition, the effect of various parameters on the performance of an industrial stripper has been investigated.

Process setup

Figure 1 shows a schematic diagram of a conventional split-flow absorber-stripper[18]. The system consists of two columns, the absorber and the stripper (or regenerator) where both columns are packed bed type. The feed gas enters the absorber, which operates at an elevated pressure, and is contacted counter-currently with the lean liquid from the regenerator, and essentially all of the carbon dioxide is removed. The rich liquid loaded with carbon dioxide from the bottom of the absorber is first flashed nearly to 1.15 atm in a throttling valve and subsequently passes through the stripper where it is stripped counter-currently by the stream generated by boiling solution in the bottom of the stripper. As the solution flows downward through the regenerator in the counter-current mode with steam, CO_3 is stripped from the solution. A portion of the lean solution from the regenerator is cooled and fed into

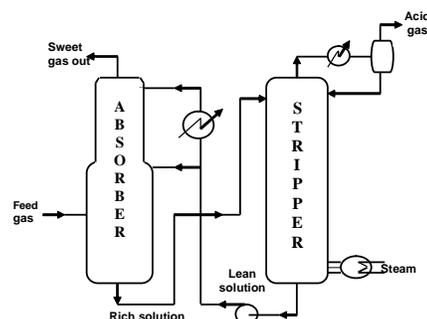**Figure 1: Schematic diagram of a conventional split-flow absorber-stripper arrangement**

TABLE 1 : Characteristics of the stripping tower, packing, reboiler and system for CO_2 desorption[18].

| Parameters	Value	units
Height of packing	26	m
Diameter of packed bed	5.5	m
Packing size (d_p)	40	mn
Packing shape	metal mini rings	-
Specific surface of packing (a)	123	mn^{-1}
Packing void fraction	0.975	-
Reboiler heat load	15.60×10^7	kJh^{-1}
Boiling point of solution in reboiler	401	K
Stripper pressure	1.15	atm

the top of the absorber while the major portion is added at a point below the top without any change in temperature. This simple modification, which is called split-flow process, raises the temperature of the rich liquid and lowers the amount of heat needed for heating the solution to the regeneration temperature. The acid gases together with some water vapor pass overhead from the stripper and through a condenser. TABLE 1 shows the characteristics and specification of a typical industrial stripping column and reboiler[18].
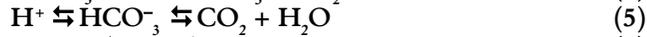
Chemical reactions

The basic reaction chemistry for decomposion of $KHCO_3$ is represented by the following reversible reaction[19,20]:

$$2\,KHCO_3 \leftrightarrows CO_2 + K_2CO_3 + H_2O \tag{1}$$
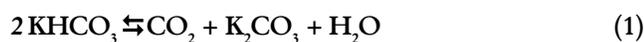
Since potassium carbonate and bicarbonate are both strong electrolytes, it may be assumed that the metal is present only in the form of K^+ ions, so reaction (1) may be more realistically represented in the ionic terms as:

$$2\,KHCO_3^- \leftrightarrows CO_2 + CO_3^{-2} + H_2O \tag{2}$$
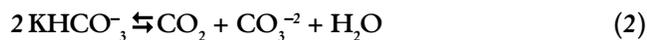
The above reaction is evidently made up of a sequence of elementary steps [19]:

$$HCO_3^- \leftrightarrows CO_2 + OH^- \tag{3}$$
$$HCO_3^- \leftrightarrows OH^- \leftrightarrows CO_3^{-2} + H_2O \tag{4}$$
$$H^+ \leftrightarrows HCO_3^- \leftrightarrows CO_2 + H_2O \tag{5}$$
$$HCO_3^- \leftrightarrows CO_3^{-2} + H^+ \tag{6}$$
$$H^+ + OH^- \leftrightarrows H_2O \tag{7}$$

Reactions (4) through (7) are fast while reaction (3) is slow and, hence, the rate controlling step, with the following rate equation[14, 19, 21]:

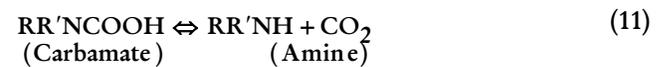$$r_{OH} = k_{OH}[OH^-]([CO_2]e - [CO_2]) \tag{8}$$

where K_{OH} is the backward rate constant and $[CO_2]_e$ is the equilibrium concentration of CO_2. Carbonate-bicarbonate system is a buffer solution, thus the concentration of the OH−ion in the solution near the surface of the liquid is not significantly depleted by the absorbed CO_2. In this case, the carbon dioxide undergoes a pseudo-first order reaction and Eq. (8) may be rewritten as[14, 16, 21]:

$$r_{OH} = k_1([CO_2]_e - [CO_2]) \tag{9}$$

Where k_1 denotes an apparent first-order rate constant.

When a small amount of amine is added into the solution, the desorption rate of carbon dioxide is enhanced greatly according to the following reactions[14]:

$$\underset{(Amine)}{HCO_3^-} + RR'NH \Leftrightarrow \underset{(Carbamate)}{RR'NCOOH} + OH^- \tag{10}$$

$$\underset{(Carbamate)}{RR'NCOOH} \Leftrightarrow \underset{(Amine)}{RR'NH} + CO_2 \tag{11}$$

At higher temperatures industrial operating conditions, the rate of reaction (11) increases significantly. As such, the system is better represented by the homogeneous catalysis mechanism [14, 20-23] and, hence, reaction (10) becomes the rate-controlling step. Using this approach in deriving Eq. (9) results in the following pseudo-first order rate equation for r_{AM}[21]:

Where k_2 is an apparent first-order rate constant.

Adding Eqs. (9) and (12) leads to the overall pseudo-first order rate equation for carbon dioxide with promoted hot potassium carbonate in liquid phase:

$$r_{Am} = k_{Am}[Am]([CO_2]_e - [CO_2]) = k_2([CO_2]_e - [CO_2]) \tag{12}$$

Where k_2 is an apparent first-order rate constant.

Adding Eqs. (9) and (12) leads to the overall pseudo-first order rate equation for carbon dioxide with promoted hot potassium carbonate in liquid phase:

$$r = (k_{OH}[OH^-] + k_{Am}[Am])([CO_2]_e - [CO_2])$$
$$= k([CO_2]_e - [CO_2]) \tag{13}$$

Where k is the overall apparent first-order rate constant and defined as:

$$k = (k_{OH}[OH^-] + k_{Am}[Am]) \tag{14}$$

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The governing equations of the model for a packed stripper [24] can be derived by carrying out the material and energy balance around a differential height of the column shown in Figure2. The envelope III is an elemental volume in the differential packed height (Δh) of the stripper, consisting of the gas and liquid phases denoted by envelops I and II, respectively. In developing the model equations we assume steady-state conditions and negligible pressure drop along the bed. It is also assumed that CO_2 and H_2O are the only components transported across the interface and the reboiler in the stripper can be modeled as a well-mixed equilibrium stage.

Mass balance
1. Gas phase

A differential mole balance in the gas phase around (dh) provides a differential equation for the gas flow along the bed:

$$\frac{dG}{dh} = (N_{CO_2} - N_{H_2O})a \tag{15}$$

Where G is superficial molar velocity of gas, NC_20 and NH_2O are mass transfer fluxes of CO_2 and H_2O, and α is the specific surface area of packing.

A differential mole balance in the gas phases for CO_2 and H_2O also gives the following differential equations for mole fraction of carbon dioxide and water in the gas phase:

$$\frac{dy_{CO_2}}{dh} = \frac{\left(N_{H_2O}y_{CO_2} + N_{CO_2}(1 - y_{CO_2})\right)a}{G} \tag{16}$$

$$\frac{dy_{H_2O}}{dh} = \frac{-\left(N_{CO_2}y_{H_2O} + N_{H_2O}(1 - y_{H_2O})\right)a}{G} \tag{17}$$
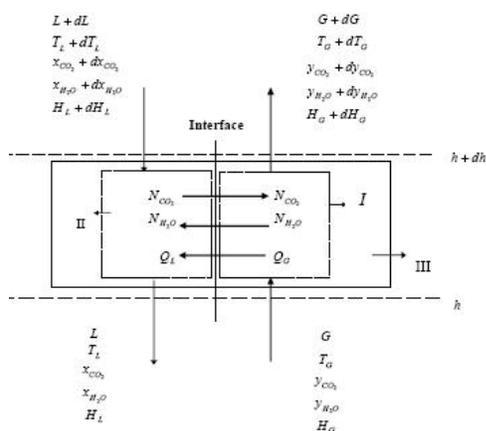

Figure 2: Differential section of packed stripper

2. Liquid phase

Here it has been assumed that for the amine-promoted carbonate solution the reaction is fast and hence the reaction take place at the same rate at which the carbon dioxide is desorbed[20, 21, 23]. A differential mole balance in the liquid phase results in:

$$\frac{dL}{dh} = -N_{H_2O}a \tag{18}$$

where L is the superficial molar velocity of the liquid. In derivation of Eq. (18) the CO_2 generated by reaction (1) is assumed to be desorbed from the liquid phase, so that the reaction (1) has no effect on the change of liquid molar flow rate.

The differential moles balance for K_2CO_3 in the liquid phase gives:

$$\frac{d(Lx_{K_2CO_3})}{dh} = -N_{CO_2}a \tag{19}$$

Replacing dL by Eq. (18) gives rise to the equation for mole fraction of K_2CO_3:

$$\frac{dx_{K_2CO_3}}{dh} = \frac{\left(N_{H_2O}x_{K_2CO_3} - N_{CO_2}\right)a}{L} \tag{20}$$

Mole balances for $KHCO_3$ and H_2O also yield the following equation in the liquid phase:

$$\frac{dx_{KHCO_3}}{dh} = \frac{\left(N_{H_2O}x_{KHCO_3} + 2N_{CO_2}\right)a}{L} \tag{21}$$

$$\frac{dx_{H_2O}}{dh} = \frac{-\left(N_{H_2O}(1 - x_{H_2O}) + N_{CO_2}\right)a}{L} \tag{22}$$

Concentration of ions and free CO_2

In the present study, the concentration of hydroxyl, carbonate, bicarbonate ions, and free CO_2 are obtained by chemical equilibrium and charge balance [15,16,23,26]. The parameter which is usually employed to describe the liquid-phase composition is the fractional saturation defined as[22]:

$$\alpha = \frac{[HCO_3^-]}{[K^+]} = \frac{[HCO_3^-]}{2m} \tag{23}$$

where m is the molarity of the solution (i.e. the total K_2CO_3 concentration[16,25-27]).

The law of electrical neutrality suggests that:

$$2[CO_3^{2-}] + [HCO_3^-] = [K^+] \tag{24}$$

Replacing $[HCO_3^-]$ by Eq. (23) give rise to the following equation for concentration of carbonate ion[22,27]:$[HCO_3^-]$

$$[CO_3^{2-}] = m(1-\alpha) \tag{25}$$

In a carbonate-bicarbonate mixture the concentration of hydroxyl ion depends on the ratio of carbonate to bicarbonate and is given by the following expression [16, 25, 28]:

$$[OH^-] = \frac{K_W}{K_6} \frac{[CO_3^{2-}]}{[HCO_3^-]} \tag{26}$$

Where K_W is the stoichiometric equilibrium constant of water and K_6 is the second dissociation constant for carbonic acid in reaction (6).

Substituting Eqs. (23) and (25) into Eq. (26) give rise to the following equation for the concentration of hydroxyl ion as a simple function of α [26]:

$$[OH^-] = \frac{K_W}{K_6} \frac{1-\alpha}{2\alpha} \tag{27}$$

According to Eqs. (5), (6), (23) and (25), the equilibrium concentration of free CO_2 in liquid is given by [16, 22, 23, 25]:

$$[CO_2]_e = 4m \frac{K_6}{K_5} \frac{\alpha^2}{1-\alpha} \tag{28}$$

Where K_5 is the first dissociation constant for carbonic acid in reaction (5).

Since potassium carbonate and bicarbonate are both strong electrolytes, combining Eqs. (23) and (24), results in the following relationship for α:

$$\alpha = \frac{x_{KHCO_3}}{x_{KHCO_3} + 2 x_{K_2CO_3}} \tag{29}$$

where $X_{K_2CO_3}$ and X_{KHCO_3} are mole fractions of potassium carbonate and bicarbonate, respectively.

Energy balance

A differential energy balance for the gas and liquid phases around the differential height(dh), gives rise to the following differential equations for the temperatures of the gas and liquid phases:

$$\frac{dT_g}{dh} = \frac{(N_{H_2O}-N_{CO_2})aT_g}{G} + \frac{(N_{CO_2}C_{PCO_2}T_L - N_{H_2O}C_{PH_2O}T_g)a}{GC_{PG}}$$
$$- \frac{h_g a(T_g - T_L)}{GC_{PG}} \tag{30}$$

$$\frac{dT_L}{dh} = \frac{N_{H_2O} aT_L}{L} + \frac{(N_{CO_2}C_{PCO_2}T_L - N_{H_2O}C_{PH_2O}T_g)a}{LC_{PL}}$$
$$- \frac{h_g a(T_g - T_L)}{GC_{PG}} + \frac{(N_{CO_2}\Delta CO_2 - N_{H_2O}\Delta H_2O)a}{LC_{PL}} \tag{31}$$

Reboiler

Heat is supplied to the column by steam coils installed in the reboiler. Since the amount of heat needed to rise the temperature of the solution leaving the reboiler is insignificant, all of the thermal energy is consumed to evaporate water which leaves the reboiler as vapor [20]. Hence:

$$G_R = \frac{Q_R}{H_{Vapor}} \tag{32}$$

where Q_R is molar flow rate of water vapor leaving the reboiler, Q_R the amount of heat which is supplied by condensation of steam in the steam coils, and H_{Vapor} the enthalpy of superheated steam leaving the reboiler given by [29, 31]:

$$H_{Vapor} = \Delta H_{H_2O}\big|_{T_{ref}} + C_{P_{vapor}}(T_R - T_{ref}) \tag{33}$$

in which, H_{ref} is the heat of vaporization of water at T_{Ref}, CP_{VAPOR} the molar specific heat of vapor, and T_R the boiling point of solution in reboiler.

Mass transfer

In this work the combined effect of mass transfer and chemical reaction is treated by Danckwerts's surface-renewal penetration theory.

According to this model the rate of mass transfer of CO_2 in the liquid phase [23,28] is governed by:

$$N_{CO_2} = E k_L (C_{CO_{2e}} - C_{CO_{2i}}) \tag{34}$$

where $C_{CO_{2i}}$ is the concentration of carbon dioxide at the interface, $C_{CO_{2E}}$ the equilibrium concentration of un-reacted carbon dioxide in the bulk of liquid, K_L the physical mass transfer coefficient, and E the enhancement factor defined as the ratio of the rate of desorption of CO_2 in the presence of chemical reaction to that obtained from physical desorption[23,25,27]:

$$E = \sqrt{1 + \frac{D_{L_{CO_2}} k_{OH}[OH^-] + D_{L_{CO_2}} k_{Am}[Am]}{k_L^2}} \tag{35}$$

The rate of mass transfer of carbon dioxide in

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the gas phase is as follows:

$$N_{CO_2} = k_{g_{CO_2}} (P_{CO_{2i}} - P_{CO_2})$$ (36)

where Kg_{CO_2} is gas phase mass transfer coefficient of carbon dioxide. Eq. (36) can be rewritten in terms of the physical solubility of CO_2 in the reactive K_2CO_3 solution as:

$$N_{CO_2} = \frac{k_{gCO_2}}{H}(C_{CO_2i} - C_{CO_2})$$ (37)

Using both gas and liquid side resistances, and combining Eqs. (34) and (37) followed by eliminating the interface partial pressure of CO_2, one can reach to the following equation for the desorption rate [23,27]:

$$N_{CO_2} = \frac{k_{gCO_2}k_L E}{k_{gCO_2} + k_L E H} = K_{L_{CO2}}(C_{CO_2e} - C_{CO_2})$$ (38)

where $KLCO_2$ is overall liquid phase mass transfer coefficient of carbon dioxide [25,30].

Because vapor is a saturated steam and the temperature of vapor is more than the temperature of liquid at all points, steam is condensed to liquid phase across the interface. Therefore the mass transfer rate of water per unit interfacial area is:

$$N_{H_2O} = \frac{h_C \Delta T}{\Delta H_{H_2O}}$$ (39)

where h_c is condensation heat-transfer coefficient [32], $\Delta H H_2O$ heat of vaporization of water, and ΔT the temperature difference between vapor and liquid phase.

Equilibrium, kinetic and transport parameters

The kinetic parameters of different amines and the equilibrium and transport parameters are tabulated in TABLES 2 and 3.

Numerical solution

The Eqs. (15)-(22) and Eqs. (30) and (31) form a set of nine differential equations which are solved numerically using an iterative approach and by taking into account the appropriate boundary conditions. First using specification of the reboiler, T_R and Q_R, the flow rate and temperature of the gas phase exiting from the reboiler and entering the column at its bottom is determined. While the flow rate, the concentration and the temperature of the liquid phase entering the top of the column are known, to start

TABLE 2 : Rate constants of reaction between amines and CO_2 where T is liquid temperature (K)

Amine	k_{AM}(m^3 kmol^{-1} h^{-1})	Ref.
DEA	6.4×10^8 exp [14.97(1 − 353/T]	[17,28]
MEA	3.4×10^8 exp [13.54(1 − 353/T]	[17,28]
TEA	$36 \times 10^{(12.72 − 2688/T)}$	[17,28]
MAE	12×10^8 exp [13.40(1 − 353/T]	[17,28]

the integration procedure, the flow rate, concentration and temperature of the liquid phase at the bottom of the column must to be guessed initially. With these guesses the column equations can be then integrated using the Euler method up to the top of the column. The results obtained from the calculations are, in turn, used for further iteration until a converged solution is obtained. The shooting method was employed in this study to verify the convergence of the solution [33,34].

For this purpose, two values of $X_b^{(1)}$ and $X_b^{(2)}$ are assumed for each of the liquid phase properties at the bottom (liquid flow rate, L, liquid temperature, T_L, and liquid mole fractions, XK_2CO_3, $XKHCO_3$, XH_2O, X_{DEA} and $XKVO_3$). The corresponding calculated values at the top of the column, $X_t^{(1)}$ and $X_b^{(2)}$, are used to calculate the difference functions, $X_t - X_t^{(1)}$ and $X_t - X_t^{(2)}$ (where X_t, is the observed liquid property at the top). The points A and B are plotted at $(X_b^{(2)}, X_t - X_t^{(1)})$ and $(X_b^{(2)}, X_t - X_t^{(2)})$ on a **xy** plane. Then the line **AB** is extended to intersect with the x axis at C, which provides the next guess for X_b, say $X_b^{(3)}$ [34] calculated using the following equation:

$$X_b^{(3)} = \frac{X_b^{(2)} - X_b^{(1)}}{X_t^{(1)} - X_t^{(2)}}(X_t^{(1)} - X_t) + X_b^{(1)}$$ (40)

A computer program has been written in Fortran language using the above procedure. A step size of 1/100 of the packed height was found to be adequate to achieve a converged solution with a reasonable level of accuracy.

Model validation

A verification of the model was carried out by comparison with the operating data of an industrial hot carbonate regeneration from Shiraz Petrochemical Complex [18] (see TABLE 1). The predicted results and actual data are presented in TABLE 4. Overall, for all the cases studied a satisfactory agree-

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ment was achieved.

RESULTS AND DISCUSSION

The performance of the carbon dioxide desorption was investigated by conducting desorption simulations under the design and operating conditions summarized in TABLES 1 and 4. The simulation results were plotted and the effects of different parameters on the desorption performance were examined.

The concentration of components in the liquid phase changes along the stripper column due to the desorption of CO_2 from solution. The mole fraction profiles for K_2CO_3, $KHCO_3$ and H_2O in liquid phase are represented in figure 3. Since $KHCO_3$ is consumed due to reaction, the concentration of $KHCO_3$ in the solution decreases as it moves down the column. Water concentration profile is affected by water vapor condensation and water generation by the liquid phase reaction. According to these effects, the concentration of water increases along the column from top to bottom. Since K_2CO_3 is a reaction product its concentration increases as the liquid moves down the column.

The temperature profiles have been calculated by using the model along the packed bed as shown in Figure 4. The gas temperature decreases as it moves

TABLE 4 : Comparison of calculated results with the observed plant data [18] under the specification indicated in TABLE 1.

Parameters	Inlet	Outlet observed	Calculated	Error %
Liquid emperature (K):	388	401	398.5	0.62
Liquid flow rate (kmol/h):	63660	61677	61179	0.81
Liquid composition (mole fraction):				
K_2CO_3	0.01260	0.03663	0.03812	-4.06
$KHCO_3$	0.07110	0.02527	0.02456	2.81
WATER	0.90766	0.9294	0.9277	0.18
DEA	0.00717	0.00722	0.00746	-3.32
KVO_3(anti-corrosion)	0.00144	0.00145	0.00149	-2.76
Gas temperature(K)	401	379	391.82	-3.38
Gas flow rate (kmol/h)	3990	3950	4210	-6.6
Gas composition (mole fraction):				
CO_2	0.0	0.3645	0.3491	4.22
H_2O	1.0	0.6355	0.6509	-2.4
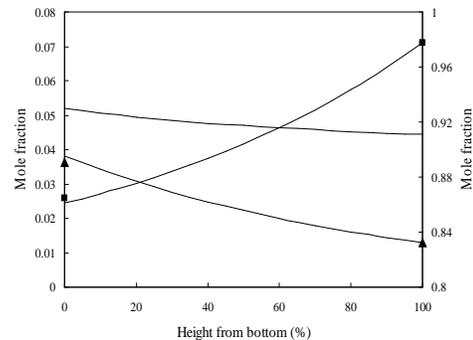
Figure 3: Concentration profile of various components in liquid phase along the packed bed

up the stripper since heat is being transferred to the liquid phase due to condensation of water vapor and the temperature difference. The absorption of heat by chemical reactions in the liquid phase is negligible in comparison with the sum of the heat which is being transferred to the liquid phase due to the condensation and temperature difference so that the liquid temperature increases as it moves down the stripper.

The absorbed CO_2 in the buffer solution of carbonate-bicarbonate is stored in the ionic form HCO_3^-. The concentration of bicarbonate ion decreases as liquid comes down from up to bottom of column due to the stripping of CO_2. Therefore, according to definition of α, carbonation ratio in the liquid phase along the length of column is decreased from top to bottom as shown in figure 5a, while concentration of $[CO_3^{2-}]$ due to chemical reaction is increased as shown in figure 5b. Concentration of OH− depends on the ratio of the concentration of carbonate to bicarbonate ion so that its concentration is increased as liquid moves down the column.
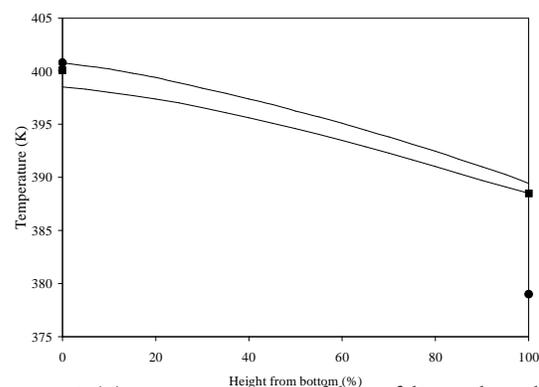
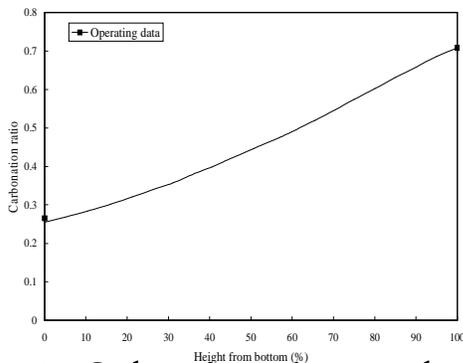**Figure 4. Temperature profiles of liquid and gas phase along the packed bed height**

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Figure 5a : Carbonation ratio versus the packed bed height

Since in a carbonate-bicarbonate mixture, HCO_3^- is consumed while $[CO_3^{2-}]$ is generated, the concentration of free CO_2, which would be in equilibrium with local concentration of HCO_3^- and $[CO_3^{2-}]$ are decreased as liquid moves down as shown in figure 5b.

In figure 6, effect of the inlet liquid temperature on separation efficiency of the stripper is studied while separation efficiency is defined as[20,23]:

$$\eta_{reg} = \frac{Q_{Co_2}}{\overset{\bullet}{m_s}} \tag{41}$$

In the above equation QCO_3 is volumes of CO_2 (m^3/h) removed, and m_S the mass flow rate of steam (kg/h) used in the reboiler. In sensitivity analysis of Figure 6 the stripper is operated so that a constant lean loading is provided.

This figure clearly shows the higher mass-transfer performance at higher inlet temperatures, which can be presented by increasing the equilibrium vapor pressure of CO_2 over the portion of solution last contacted by the gas. It is clear that at lower temperatures, the stripping curve has a horizontal
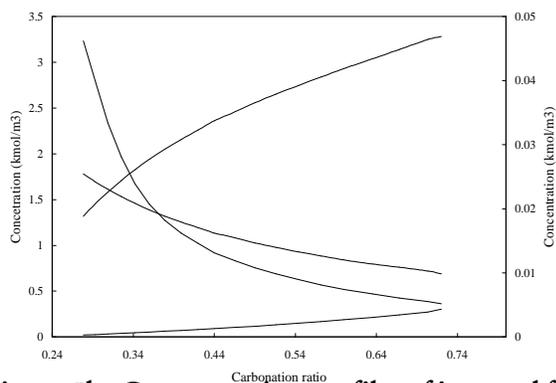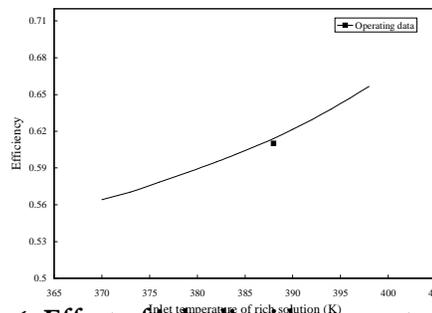

Figure 6: Effect of inlet liquid temperature on regeneration efficiency

asymptote, so a large increase in the inlet liquid temperature is required to obtain a small increase in efficiency. Hence, beside the influence of the equilibrium vapor pressure of CO_2, the steam consumption rate (m_s), which indirectly depends on the liquid temperature plays an important role on the stripping performance.

A change in the promoter concentration obviously has an impact on the desorption performance while the stripper is operated to provide a constant lean loading. According to figure 7, an increase in the amine concentration induces a higher CO_2 stripping. The possible explanation for this behavior is that increasing the amine concentration reflects the higher enhancement factor in the liquid phase, which is directly proportional to the overall KL in the case of liquid phase controlled mass transfer.

Promoter type is considered as another essential factor affecting the efficiency of CO_2 desorption process. According to figure 8 the role of four types of amines were compared for their effectiveness in carbon dioxide stripping at identical operating conditions. These were DEA, MEA, TEA and MAE. As shown in figure 8, MAE provides the highest mass
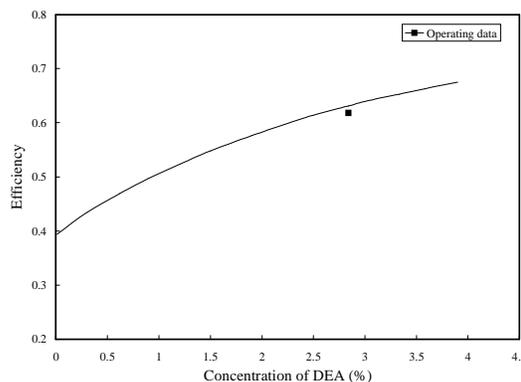

Figure 5b : Concentration profiles of ions and free CO_2 versus carbonation ratio

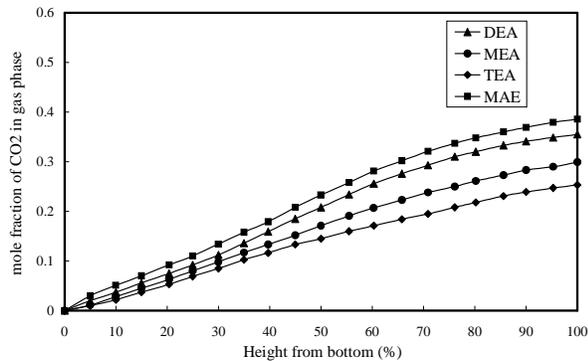**Figure 7: Effect of DEA concentration on regeneration efficiency**

Figure 8 : Effect of amine type on mole fraction of CO_3 along the column height
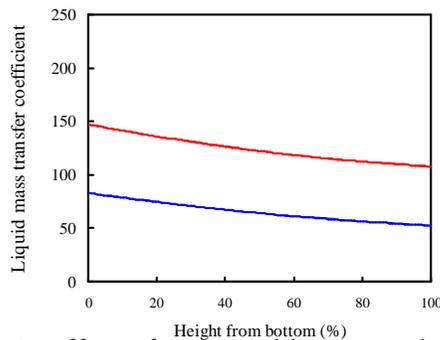

Figure 9: Effect of amine addition on the liquid phase mass transfer coefficient along the column

transfer performance when compared with MEA, TEA and DEA. The difference between the regeneration efficiency by three of the amines is preliminary influenced by the second order rate constant, k_{AM} as indicated in TABLE 2. According to this TABLE, the value of k_{AM} for the $CO_2 - MAE$ system is greater than that of $CO_2 - MAE$, $CO_2 - TEA$ and $CO_2 - DEA$, thus leading to a higher enhancement factor and regeneration efficiency.

The role of amine in the mass transfer performance is shown in figure 9. As can be seen, addition of amine to the liquid phase induces liquid phase mass transfer coefficient (k_L^E). The difference between the liquid phase mass transfer coefficients for amine and amine-free solution is preliminary influenced by the second-order rate constant, k_{AM}, as indicated by Eq. (12). An increase in k_{AM} reflects the higher enhancement factor in the liquid phase (Eq. (35)) which is directly proportional to the liquid phase mass transfer coefficient as shown in Eq. (34).

CONCLUSION

A numerical model was developed and validated for simulation of carbon dioxide desorption from promoted hot potassium carbonate in industrial-scale strippers. The proposed model accurately predicted the stripper performance when the predictions were compared with observed data. The effect of three parameters on stripper performance was investigated; inlet liquid temperature, promoter concentration and promoter type. The inlet liquid temperature was found to posses two important effects on the general behavior of the stripper. Firstly, it influences the mass transfer process and secondly the steam consumption rate of reboiler. In the stripper which is controlled by the liquid side mass transfer, the increase of E with increasing the weight percent of amine in the solution, demonstrates that the resistance in the liquid phase is decreased as amine is added to the solution. The use of other amines is an efficient way to enhance the regeneration efficiency of desorption process which has been discussed in this work. The model provides a procedure to investigate the effect of new promoters on the CO_2 desorption.

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Nomenclature

α	specific surface area (m^{-2} m^{-3})
C_k	concentration of kth component (kmol m^{-3})
C_{ke}	equilibrium concentration of kth component in the bulk of liquid (kmol m^{-3})
C_{ki}	concentration of kth component at interface (kmol m^{-3})
C_{Pg}	average molar specific heat of gas (kJ kmol m^{-1} K^{-1})
C_{Pk}	average specific heat of kth component (kJ kmol m^{-1} K^{-1})
C_{PL}	molar specific heat of liquid (kJ kmol m^{-1} K^{-1})
C_{PL}	specific heat of liquid (kJ kg^{-1} K^{-1})
D_{LCO2}	diffusivity of CO_2 in K_2CO_3 solution (m^2 m^{-1})
Dg_{CO2}	diffusivity of CO_2 in gas (m^2 h^{-1})
d_P	packing nominal size (m)
E	enhancement factor
G	molar velocity of gas (kmol m^{-2} h^{-1})

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TABLE 3 : Equilibrium, kinetics and transport parameters

parameter	expression	source
α	$\alpha = \dfrac{[K^+] - 2[CO_3^{2-}]}{[K^+]} = \dfrac{[HCO_3^-]}{[K^+]}$	[16]
$P_{H_2O_i}$	$\log P_{H_2O_i} = -(L'/2.303R)((1/T) - 2.45\times 10^{-3}) - 1.1672 + C$; $L' = 40983.6$	[34]
C	$C = 1.2014 + (0.2857/x_c) - (0.0537/x_c^2)$	[34]
x_C	$x_C = \dfrac{0.691(\% KHCO_3)}{\% K_2CO_3 + 0.691(\% KHCO_3)}$	[34]
$P_{CO_2 e}$	$P_{CO_2 e} = 2\dfrac{K_2[K^+]}{K_1 H}\dfrac{\alpha^2}{1-\alpha}$	[16]
K_5	$\log(K_5) = -(3404.7/T) + 14.843 - 0.03279T$	[16]
K_6	$\log(K_6) = -(2902.4/T) + 6.498 - 0.0238T$	[16]
H	$\log(H/H_W) = -K_S I$; $K_S = 0.06$, $I = 6.2$	[16]
H_W	$\log H_W = (1140/T) - 5.30$	[16]
k_{OH}	$\log(k_{OH}) = 13.635 - (2895/T) + 0.08I$	[35]
k_{g_k}	$\dfrac{k_{g_k} RT}{aD_{g_k}} = 5.32(\dfrac{\hat{G}}{a\mu_g})^{0.7}(\dfrac{\mu_g}{\rho_g D_{g_k}})^{1/3}(ad_p)^{-2.0}$	[23]
k_L	$k_L(\dfrac{\mu_l^2}{\rho_l^2 g})^{1/3}/D_{CO_2} = 0.015(\dfrac{\hat{L}}{a\mu_l})(\dfrac{\mu_l}{\rho_l D_{CO_2}})^{1/3}$	[36]
D_{CO_2}	$\log D_{CO_2} = -3.0188 - \dfrac{586.9729}{T} - 0.4437$	[15]
h_g	$h_g = \sum_k y_k h_{g_k}$	[37]
h_{g_k}	$h_{g_k} = k_{y_k} C_{p_k}(Le)^{2/3}$	[37]
C'_{P_L}	$C'_{P_L} = 4.1774 - 0.0382\omega - 0.4445\times 10^{-3}\omega^2 + 1.2798\times 10^{-5}\omega^3$	[20]
ΔH_{CO_2}	$\Delta H_{CO_2} = 27228.2 + 81.37\omega + 5.32\omega^2 - 0.1313\omega^3 + 1.654\times 10^{-3}\omega^4$	[38]
ω	$\omega = \dfrac{\% K_2CO_3 + 0.691(\% KHCO_3)}{\% K_2CO_3 + 0.781(\% KHCO_3) + \% H_2O}$	[22]

$\hat{G}$	mass velocity of inert gas (kg m^{-2} h^{-1})	k_{OH}	backward rate constant of reaction (3) (s^{-1})
G_R	molar velocity of vapor leaves the reboiler (kmol h^{-1})	K_g	overall mass transfer coefficient (kmol^{-1} m^{-2} atm^{-1})
H	solubility of carbon dioxide in solution (kmol atm^{-1} m^{-3})	K_y	Gas side mass transfer coefficient (kmol h^{-1} m^{-2})
		k_L	liquid side mass transfer coefficient (mh^{-1})
H_{VAPOR}	enthalpy of superheated steam (kJ kmol^{-1})	K_5	first ionization constant for carbonic acid (kmol m^{-3})
h	heat transfer coefficient in gas phase (kJ m^{-2} h^{-1} K^{-1})	K_6	second ionization constant for carbonic acid (kmol m^{-3})
h_C	condensing heat transfer coefficient (kJ m^{-2} h^{-1} K^{-1})	L	molar velocity of liquid (kmol m^{-2} h^{-1})
ΔHCO_2	heat of reaction and absorption of CO_2 (kJ kmol^{-1})	$\hat{L}$	liquid mass flow rate (kg h^{-1})
ΔHH_2O	heat of vaporization of water (kJ kmol^{-1})	Le	Lewis number
I	ionic strength of solution (kJ ion m^{-3})	N_K	mass transfer flux of kth component (kmol m^{-2} h^{-1})
k	pseudo first order rate constant (h^{-1})	P_K	partial pressure of kth component in gas phase (atm)
k_{AM}	second order rate constant of amine (m kmol^{-1} h^{-1})	N_{Ke}	equilibrium vapor pressure of kth component in gas phase (atm)
k_{OH}	forward rate constant of reaction (3) (m^{-3} kmol^{-1} s^{-1})		
k_g	Gas side mass transfer coefficient (kmolh^{-1} m^{-2} atm^{-1})		

P_{Ki}	partial pressure of kth component in in the liquid-gas interface (atm)
pr	Prantl number
Q_R	reboiler heat load (kJ h^{-1})
R	universal gas constant (m^3 atm kmol^{-1} K^{-3})
Re	Reynolds number
S	cross sectional area of column (m^2)
Tg	gas temperature (K)
T_L	liquid temperature (K)
t	liquid temperature (K)
W_v	mass velocity of vapor (kg h$^{-1)}$
X_k	mole fraction of kth component in the liquid phase
Y_k	mole fraction of kth component in the gas phase

Greek symbols

α	carbonation ratio
μg	gas phase viscosity (kg m^{-1} h^{-1})
μ_y	vapor phase viscosity (kg m^{-1} h^{-1})
μ_L	liquid phase viscosity (kg m^{-1} h^{-1})
P_g	gas phase density (kg m^{-3})
P_L	liquid phase density (kg m^{-3})
ω	total equivalent weight percent of K_2CO_3

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