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Absorption with chemical reaction: evaluation of rate promoters effect on CO_2 absorption in hot potassium carbonate solutions

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Abstract

The improving effect of rate promoters has been investigated by experiments at pilot plant scale in conditions close to the operating conditions of the top zone of a typical hot potassium carbonate industrial packed bed absorber. The evaluation of promoter enhancement factor has been done by successive experiments with absorption of CO_2 into water, into carbonate solution and into promoted carbonate solution.

Keywords: Rate promoters, hot potassium carbonate, modeling and simulation

1. Introduction

The removal of carbon dioxide from industrial gas streams is important either to meet certain process specifications, as in the case of synthesis gas (ammonia and methanol manufacturing), or to keep emission limits. Widely prevalent chemical absorption systems employ inorganic and organic aqueous solutions: hot potassium carbonate, monoethanolamine (MEA), diethanolamine (DEA) or tertiary amines as chemical sorbents.
The main advantages of carbonate solutions for CO_2 removal are the high chemical solubility of CO_2 in the carbonate/bicarbonate system and low solvent

costs. The major difficulty is a relatively slow reaction in the liquid phase causing low mass transfer rates and therefore requiring a large contact surface. In order to increase process efficiency, rate promoting additives are commonly used. The paper presents an evaluation of the effect of some of the promoters frequently mentioned in the literature: diethanolamine (DEA), 2-aminoethoxy-ethanol (AMET), triethanolamine (TEA), triethylamine (TREA) and methyl-diethanolamine (MDEA).

When carbon dioxide is absorbed into potassium carbonate/bicarbonate solution, the following exothermic reaction takes place:

$$K_2CO_3 + CO_2 + H_2O \Leftrightarrow 2\,KHCO_3 \qquad\qquad (a)$$
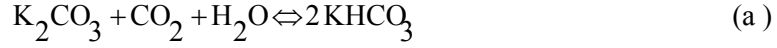
Developed initially by Benson et al. [1], hot potassium carbonate process was subject to several improvements, the most important one being the addition of some rate promoters (usually amines) that can enhance largely the absorption rate. Previous papers on amine promoted potassium carbonate have investigated several aspects of the process: most effective promoters [2], carbamate equilibrium in hot potassium carbonate [3], amines effect on desorption rate [4], equilibrium and reaction rates for DEA promoted process [5], etc. A new promoter, piperazine, has been proposed recently and its effect on hot potassium carbonate process has been extensively investigated by Hilliard [6] and Cullinane [7].

2. Experimental setup

Within this work, in order to better account for promoters' effect on mass transfer rate, successive experiments with absorption of CO_2 into water, into carbonate solution and into promoted carbonate solution have been carried out at pilot plant scale.

Pilot plant geometric properties and its hydrodynamic parameters have been extensively investigated in a previous paper by Pröll et al. [8]. Because the thermal effects occurring together with absorption show only little impact at pilot plant size, the steady-state mathematical model is based on differential mass balances only. In equations (1) and (2), the extent of axial dispersion is described by the dimensionless Peclet number and the well known boundary conditions by Danckwerts have been used for each phase.

$$-\frac{\partial Y}{\partial z} + \frac{1}{Pe_G} \cdot \frac{\partial^2 Y}{\partial z^2} - \frac{K_G \cdot a \cdot H}{G_0} \cdot \left(p_{CO_2} - p_{CO_2}^*\right) = 0 \qquad\qquad (1)$$

$$\frac{\partial X}{\partial z} + \frac{1}{Pe_L} \cdot \frac{\partial^2 X}{\partial z^2} + \frac{K_G \cdot a \cdot H}{\rho \cdot L_0} \cdot \left(p_{CO_2} - p_{CO_2}^*\right) = 0 \qquad\qquad (2)$$

In order to evaluate the actual interfacial area and the physical mass transfer parameters, steady state absorption experiments have been carried out using pure water. In a next step, the chemical absorption model (kinetics, equilibrium) has been validated by experiments with absorption into carbonate solution. The promoters' effect on reaction rate has been evaluated on the basis of separate experiments for each case. The gas concentration is measured (CO_2 analyzer) at the gas entry, in the middle of the column between the two packing sections and at the gas exit at the top of the column. For chemical absorption experiments, CO_2 loading in liquid phase has been evaluated by chemical analysis at the inlet and outlet of the solution.

3. Results and discussion

Steady state absorption experiments for the **physical absorption of CO_2 into water** have been carried out at temperatures of 40 to 65°C, specific flow rates of inert gas between 9.0 and 12.5 kmol/(m²·h), specific flow rate of water between 12.5 and 20.0 m³/(m²·h) and an absolute pressure up to 5 bar.

The results indicate that the estimation methods for the physical mass transfer parameters k_G, k_L^0, and a, taken from Onda [9], are able to describe the behavior of the pilot plant. Three different expressions for Henry constant temperature dependence were tested versus experimental predictions of CO_2 solubility and, finally [10], the relation (7), used also by Suenson [11], has been chosen as best fitted dependence.

In the case of **chemical absorption**, the Danckwerts criterion for a pseudo-first order kinetics has been accomplished for all experiments. All steady state experimental results were tested for CO_2 mass balance (gas phase versus solution) and, finally, eight experiments have been selected for the evaluation of the model parameters (Table 1).

Table "1. Experimental data for CO2 absorption into carbonate/bicarbonate solution"

Parameter (units)	1	2	3	4	5	6	7	8
P [bar]	4.3	4.3	4.3	5	4	4	3.7	3.7
T_c [°C]	60	61	61	65	55	58	65	66
$G_0 \cdot 10^3$ [kmol$_{inert}$/(m² · s]]	3.35	3.34	3.36	2.44	3.22	3.21	3.11	3.11
$L_0 \cdot 10^3$ [m³/(m² · s]	3.06	5.38	3.06	3.06	3.93	3.93	5.97	5.68
$Y_{IN} \cdot 10^2$ (z=0)	4.16	4.27	3.84	4.38	4.38	4.60	4.71	4.71
$Y_M \cdot 10^2$ (z=0.5)	2.04	1.57	1.94	1.26	2.67	2.46	2.02	1.85
$Y_F \cdot 10^2$ (z=1)	1.47	1.47	1.32	0.96	1.62	1.44	1.20	1.13
α_{IN} [%]	22.02	23.54	31.58	32.74	24.92	23.60	24.59	20.87
α_F [%]	24.72	25.11	34.06	35.02	27.51	26.35	26.52	22.91
Pe_L	23.49	43.25	23.88	24.44	28.09	29.57	30	30
Pe_G	28.98	10.82	28.42	24.25	22.98	21.33	20	20
E	5.45	4.16	4.47	5.29	3.52	4.19	4.64	5.55
φ_{EC}	0.97	0.89	1.32	1.06	1.10	1.13	0.99	0.89

An extensive discussion about the estimation of equilibrium and kinetic parameters is presented by Pröll [8] and, based on this analysis, the following relations have been used in the evaluation of the enhancement factor of the absorption by chemical reaction and, respectively, for CO_2 physical solubility:

$$\log k_{OH^-} = 13635 - \frac{2895}{T} + 0.08 \cdot I_i \quad (3) \qquad k_{1,app} \cong k_{OH^-} \cdot [OH^-] \quad (4) \qquad Ha = \sqrt{\frac{k_{1,app} \cdot D_L}{(k_L^0)^2}} \quad (5)$$

$$E = \frac{Ha}{\tanh(Ha)} \quad (6) \qquad He_w = 10^{\frac{-1350}{T} + 5.86} \quad (7) \qquad He = 10^{(-0.125 \cdot M)} \cdot He_w \quad (8)$$

An improvement of the mass transfer model in order to better fit measured results at different temperatures has been obtained by introducing a tuning factor which was expressed as a function of initial carbonation ratio:

$$\varphi_{EC} = 0.4782 + 2.2194 \cdot \alpha_{IN} \qquad\qquad\qquad\qquad (9)$$

In the case of the evaluation **of promoters' effect** on reaction rate, pilot plant main operating parameters have been maintained in the same limits as in the case of absorption in carbonate solutions. For all experiments, mass fraction of the promoters in the solution has been maintained to a value of around 1% (w/w). Figure 1 shows a comparison between pilot plant data and simulation results in the case of DEA promoted potassium carbonate (main operating parameters are listed in Table 2).

Table "2. Operating parameters for Figure 1 case"

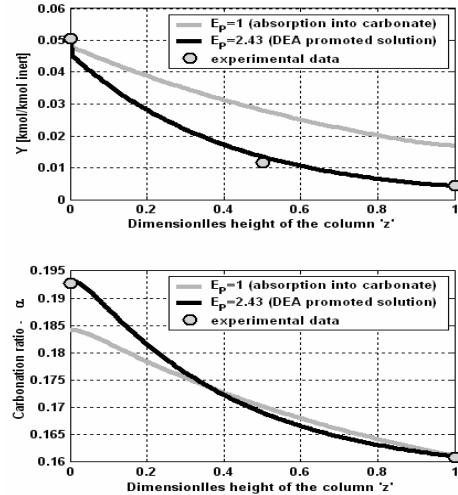| Process parameters	Values
P [bar]	3.75
T_c [°C]	59
$G_0 \cdot 10^3$ [kmol$_{inert}$/(m$^2 \cdot$ s]]	3.10
$L_0 \cdot 10^3$ [m^3/(m$^2 \cdot$ s]	3.93
$Y_{IN} \cdot 10^2$ (z=0)	5.04
$Y_M \cdot 10^2$ (z=0.5)	1.16
$Y_F \cdot 10^2$ (z=1)	0.45
α_{IN} [%]	16.08
α_F [%]	19.28
Pe_L	30.32
Pe_G	20.55
Promoter conc. [% (w/w)]	1
E	4.77
φ_{EC}	0.83

Figure 1. Carbon dioxide gas phase molar ratio and carbonation ratio in the liquid phase along the packing zone: simulation versus experimental data

Liquid side mass transfer coefficient (k_L) was computed as a product of physical absorption mass transfer coefficient (k_L^0), enhancement factor of absorption by chemical reaction (E), tuning coefficient φ_{EC} and the enhancement factor of chemical reaction by promoter (Ep):

$$k_L = E_P \cdot \varphi_{EC} \cdot E \cdot k_L^0 \tag{10}$$

The promoter enhancement factor has been evaluated on the basis of square errors minimization in order to obtain the agreement between measured and simulated pilot plant profiles. Tuned values of the promoter enhancement factor versus inlet solution carbonation ratio for all five promoters investigated during the experimental work are shown in Fig. 2.
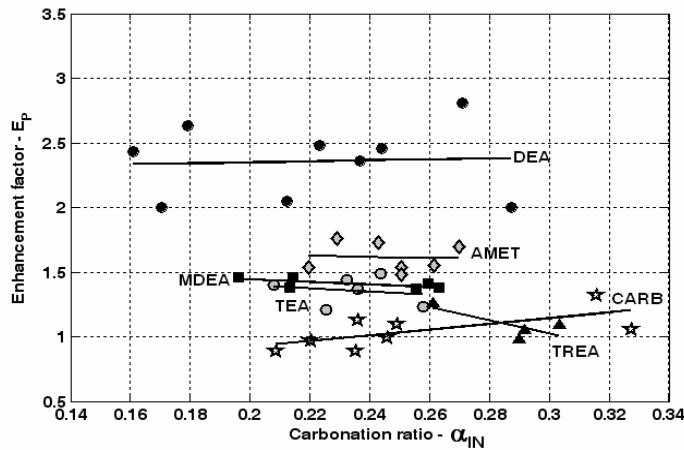

Figure 2. Tuned values of the promoter enhancement factor versus inlet solution carbonation ratio

Practically, all promoters have shown a positive effect on overall mass transfer but, in the investigated range, DEA seems to be the most effective promoter.

4. Conclusions

Within this work, an evaluation of the effect of some of the rate promoters mentioned in the literature for $K_2CO_3/KHCO_3$ solutions has been carried out by successive experiments with absorption of CO_2 into water, into carbonate solution and into promoted carbonate solution. Operational experimental conditions (partial pressure of CO_2, temperature, carbonation ratio) for the pilot plant packed bed absorber have been chosen close to the top zone of a typical industrial absorber. In the investigated experimental range, the DEA effect on the reaction rate turns out to be higher than the effect of other promoters tested.

Nomenclature

a - effective interfacial area per unit packed volume $[m^2/m^3]$

D_L – diffusion coefficient of CO_2 in solvent $[m^2/s]$

E - enhancement factor of absorption by chemical reaction;

E_p - promoter enhancement factor;

G_0 - superficial molar inert gas flow-rate (G/S) $[kmol/(m^2 \cdot s)]$;

H - total column height [m];

Ha – Hatta number;

He, He_W - physical solubility of CO_2 in the solution or water $[bar \cdot m^3/kmol]$;

$k_{1,app}$ – pseudo-first order rate constant $[s^{-1}]$;

k_L - gas or liquid side mass transfer coefficients $[kmol/(bar \cdot m^2 \cdot s)]$, [m/s];

k_L^0 - liquid side mass transfer coefficient for physical absorption [m/s];

k_{OH} - rate constants $[m^3/(kmol \cdot s)]$;

K_g - overall mass transfer coefficient $[kmol/(bar \cdot m^2 \cdot s)]$;

I_I – ionic strength

L_0 - liquid superficial velocity $[m^3/m^2 \cdot s]$;

M – equivalent K_2CO_3 solution molarity $[kmol/m^3]$;

P - total pressure [bar];

Pe_g , Pe_L - Peclet number in the gas or liquid phase;

T - absolute temperature [K];

X - molar load of CO_2 in liquid $[kmol/m^3]$;

Y - CO_2 molar ratio in the gas phase $[kmol/kmol_{inert}]$;

z - distance from the bottom of the packing, normalized with column height;

α - carbonation ratio, $[HCO_3^-]/[K^+]$;

φ_{EC} – tuning coefficient;

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