

# Absorption of Carbon Dioxide with Hot Potassium Carbonate Solution: Modeling and Statistical Analysis of Known Experimental Data

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The process of absorbing carbon dioxide with an aqueous solution of hot potassium carbonate is widely used in industry for gas purification. The results of numerical modelling of the process are compared with a limited set of experimental data in well-known works. In this paper, a mathematical model of the process in a packed absorber is developed; fitting parameters are taken on the basis of processing known experimental data. The model is based on the equations of heat and mass transfer. Main characteristics: concentrations of substances and temperatures in the liquid and gas phases, depend on one coordinate  $z$  directed along the height of the absorber. The heat and mass transfer coefficients were calculated using the Onda formulas. The  $\text{CO}_2$  equilibrium at the liquid-gas interface was determined by Sechenov relation. The adequacy of the model was checked by comparing the calculations of carbon dioxide concentration along the absorber with the known experimental data not included in the sample from which the model parameters were determined. The numerical dependences of the  $\text{CO}_2$  content in the scrubbed gas on the physical characteristics of the process are obtained.

## 1. Introduction

An analysis of early work on modeling  $\text{CO}_2$  absorption by hot potash solution was presented in Sanyal et al. (1988). It is noted that the models are not strict; data in the open literature are limited. Sanyal et al. (1988) simulated the absorption process of hot potassium carbonate solution promoted by diethanolamine (DEA). The calculation data was compared with experiments at two pilot plants. Rahimpur and Kashkooli (2004) used a close model of carbon dioxide absorption by hot potassium carbonate, using monoethanolamine (MEA), methyl diethanolamine (MAE), diethylenetriamine (DTA) as promoters. The influence of the concentration of promoters on the efficiency of the process was evaluated. Both in Sanyal et al. (1988) and in Rahimpour and Kashkooli (2004), the calculations were compared with a limited set of experimental data, outdated data on the kinetics of the process were used. In a later work of Smith et al. (2015),  $\text{CO}_2$  absorption was studied experimentally with potash supplemented with glycine as a promoter. In the work of Hu et al. (2017), promoters including boric acid, potassium glycinate, potassium proline, potassium sarcosinate and a thermally stable carbonic anhydrase enzyme have been studied. Recently, precipitating solvents have been used to clean  $\text{CO}_2$  from gases, which allows one reaction product to be removed from the liquid, shifting the reaction equilibrium and increasing the mass transfer of  $\text{CO}_2$  from the gas phase to the liquid phase (Moioli et al., 2019).

Modeling of absorption processes in recent works was based on the use of Aspen Plus. However, comparison of calculations with experimental data was fragmented. The calculations performed do not allow us to assess the influence of the physical characteristics on the  $\text{CO}_2$  content in the purified gas.

The aim of the work is to construct a mathematical model of the process of  $\text{CO}_2$  absorption by an aqueous solution of hot potash in a packed absorber based on known experimental data, and to estimate the  $\text{CO}_2$  content in the purified gas depending on the physical characteristics of the process.

## 2. The mathematical model of the process

The gas purification process takes place in a packed absorption apparatus. An aqueous solution containing  $K_2CO_3$  and  $KHCO_3$  enters from above. The cleaned gas containing carbon dioxide, water vapor and nitrogen enters the absorber in countercurrent flow from below. The height of the absorber is much larger than its diameter, all the characteristics of the process — the concentrations of components in the liquid and gas phases, as well as the temperatures of the phases — depends on one vertical coordinate  $z$ .

Carbon dioxide is absorbed by the liquid and reacts chemically.



As a result, the  $CO_2$  content in the gas decreases, i.e. it is being cleaned (Danckwerts, 1970). Reaction (1) can be represented as a set of elementary reactions for ions. According to Hikita et al. (1976), the rate of a process is determined by the reaction



For low concentrations (ideal solutions), the chemical reaction rate is

$$r = k_{OH} [OH^-] ([CO_2] - [CO_2]_e) \quad (3)$$

where  $k_{OH}$  is the reaction rate constant, the brackets  $[\ ]$  indicate the concentration of the components in the solution,  $kmol/m^3$ , and the subscript  $e$  corresponds to the equilibrium concentration.

Gondal et al. (2016) gives the following estimate of the constant

$$\ln k_{OH} = 26.437 - 5111.2/T[K]; [m^3 / (kmol \times s)]. \quad (4)$$

The main resistance to the transfer of carbon dioxide at the gas-liquid interface is concentrated in the liquid phase. The interphase  $CO_2$  flux  $N_1$ ,  $kmol/m^2/s$ , can be represented as

$$N_1 = k_1 ([CO_2]_s - [CO_2]_e) \quad (5)$$

where  $[CO_2]_s$  is the concentration of carbon dioxide in the liquid near the boundary,  $k_1$  is the mass transfer coefficient,  $m/s$

$$[CO_2]_e = p_1 e^{p_2(T-T_0)} [CO_2]_e^{id}; T_0 = 373 K; [CO_2]_s = \frac{y_1 P}{H_{CO_2}}; k_1 = p_3 (D_{CO_2} k_{OH} [OH^-]_e^{id})^{1/2}. \quad (6)$$

$[CO_2]_e^{id}$ ,  $[OH^-]_e^{id}$  - estimates of the equilibrium concentrations for ideal solutions at given concentrations of  $K_2CO_3$  and  $KHCO_3$ . The latter was calculated using the Edwards formulas (Edwards et al., 1978). The model parameters,  $p_1$ ,  $p_2$ ,  $p_3$  take into account the non-ideal solution,  $y_1$  is the mole fraction of  $CO_2$  in the gas phase,  $P$  is pressure, MPa,  $H_{CO_2}$  is solubility of carbon dioxide in ionic solutions,  $MPa \times m^3/kmol$ . The solubility in water was calculated according to Carroll et al. (1991), the influence of ions was taken into account according to Sechenov's formula (Weisenberger and Shumpe, 1996),  $D_{CO_2}$  is the diffusion coefficient of carbon dioxide in the liquid phase,  $m^2/s$ . For  $p_3 = 1$ , the expression for the mass transfer coefficient corresponds to the well-known Danckwerts formula (Danckwerts, 1970).

The mass conservation equations for gas and liquid flows are consistent with the Rahimpour and Kashkooli (2004) model. In the gas phase, the equations are as follows

$$\frac{dG}{dz} = -(N_1 M_{CO_2} + N_2 M_{H_2O})a; \quad \frac{dG_1}{dz} = -N_1 M_{CO_2}a; \quad \frac{dG_2}{dz} = -N_2 M_{H_2O}a; \quad G = G_1 + G_2 + G_3 \quad (7)$$

Here  $G$  is the mass flow rate of gas,  $kg \cdot m^2/s$ ,  $G_1$ ,  $G_2$ ,  $G_3$ , the mass flow rate of carbon dioxide, water vapor and nitrogen.  $N_2$  is the molar flux of water vapor at the liquid-gas interface.  $M_{CO_2}$ ,  $M_{H_2O}$  are molar masses,  $kg/kmol$ ,  $a$ , is the specific surface area,  $m^1$ . The flux density  $N_1$  is calculated by the Eq(5). The resistance to  $H_2O$  transfer is concentrated in the gas phase, the flux  $N_2$  is equal to

$$N_2 = k_{g2} (y_2 P - P_{H_2Oe}) \quad (8)$$

Where  $y_2$  is mole fraction of water vapour,  $k_{g2}$ ,  $kmol/m^2/s/MPa$ , is the mass transfer coefficient of  $H_2O$ ,  $P_{H_2Oe}$  is the equilibrium pressure of water vapor.

In the liquid phase there are equations:

$$\frac{dL}{dz} = (N_1M_1 - 2N_2M_2)a; \quad \frac{dL_1}{dz} = N_1M_1a; \quad \frac{dL_2}{dz} = -2N_2M_2a; \quad L = L_1 + L_2 + L_3 \quad (9)$$

Here L is the mass flow rate of the liquid, kg/m<sup>2</sup>/s, L<sub>1</sub>, L<sub>2</sub>, L<sub>3</sub> are the mass flow rates of K<sub>2</sub>CO<sub>3</sub>, KHCO<sub>3</sub> and H<sub>2</sub>O, M<sub>1</sub>, M<sub>2</sub>, M<sub>3</sub> are their molar masses.

The expressions for the molar flow rates Gm<sub>k</sub>, kmol/m<sup>2</sup>/s, and molar fractions y<sub>k</sub> in the gas phase are as follows:

$$Gm_1 = \frac{G_1}{M_{CO_2}}; \quad Gm_2 = \frac{G_2}{M_{H_2O}}; \quad Gm_3 = \frac{G_3}{M_{N_2}}; \quad (10)$$

$$Gm = Gm_1 + Gm_2 + Gm_3; \quad y_k = \frac{Gm_k}{G}; \quad k=1,2,3.$$

Here M<sub>N2</sub> is molar mass of nitrogen.

Mass fractions in the liquid phase are equal to:

$$c_k = \frac{L_k}{L}, \quad k = 1, 2, 3. \quad (11)$$

The energy equations are as follows:

$$\frac{d}{dz}(T_g) = -\frac{Qa}{G^*c_{pg}} + \frac{(N_1M_{CO_2} + N_2M_{H_2O})a(T_g - T_s)}{G} \quad (12)$$

$$\frac{d}{dz}(T_L) = -\frac{Qa}{L^*c_{pL}} - \frac{(N_1M_{CO_2}\Delta H_{CO_2} + N_2M_{H_2O}\Delta H_{H_2O})a}{L^*c_{pL}} \quad (13)$$

Here, T<sub>g</sub> and T<sub>L</sub>, are the temperatures, K, in the gas and liquid phases, T<sub>s</sub> is the temperature at the interface, ΔH<sub>CO2</sub> is the specific heat of dissolution and CO<sub>2</sub> reaction, kJ/kmol. ΔH<sub>H2O</sub> is the specific heat of evaporation of water, c<sub>pL</sub> and c<sub>pg</sub> are the specific heat of liquid and gas, kJ/kg/K. Q is the heat flux density at the liquid-gas interface, kJ/m<sup>2</sup>/s

$$Q = h_g(T_g - T_s) = h_L(T_s - T_L); \quad T_s = \frac{T_g h_g + T_L h_L}{h_g + h_L} \quad (14)$$

h<sub>g</sub> and h<sub>L</sub> are heat transfer coefficients in the gas and liquid phases, kJ/m<sup>2</sup>/s/K. The analogy between heat and mass transfer (Frank-Kamenetskii and Thon, 1955) was used to calculate them.

$$h_g = \sum_k y_k h_{gk}; \quad h_{gk} = k_{gk} \bar{c}_{pk} (Le_k)^{2/3}; \quad h_L = k_L \rho_L c_{pL} Le_L^{1/2}; \quad (15)$$

Here,  $\bar{c}_{pk}$  are the molar heat capacities of the components in the gas phase, kJ/kmol/K, Le is the Lewis number, k<sub>gk</sub>, kmol/m<sup>2</sup>/s/MPa, and k<sub>L</sub>, m/s, are the mass transfer coefficients in the gas and liquid phases. The latter were calculated by Onda correlations (1968). In the gas phase

$$\frac{k_{gk} RT_g}{aD_{gk}} = 2.00 \left( \frac{G}{a\mu_g} \right)^{0.7} \left( \frac{\mu_g}{\rho_g D_{gk}} \right)^{1/3} (ad_p)^{-2}, \quad k = 1, 2, 3 \quad (16)$$

where D<sub>gk</sub> are the diffusion coefficients of the components in the gas phase, m<sup>2</sup>/s, μ<sub>g</sub> is the gas viscosity, kg/m/s, ρ<sub>g</sub> is the gas density, kg/m<sup>3</sup>, R is the universal gas constant, d<sub>p</sub> is the packing nominal size, m. In the liquid phase

$$k_L \left( \frac{\rho_L}{\mu_L g} \right)^{1/3} = 0.0051 \left( \frac{L}{a\mu_L} \right)^{2/3} \left( \frac{\mu_L}{\rho_L D_L} \right)^{-1/2} (ad_p)^{0.4} \quad (17)$$

where, μ<sub>L</sub> is the liquid viscosity, ρ<sub>L</sub> is the liquid density.

The boundary conditions are as follows:

$$G = G_{start}; G_1 = G_{1start}; G_2 = G_{2start}; T_G = T_{Gstart}, \text{ for } z = 0 \quad (18)$$

$$L = L_{start}; L_1 = L_{1start}; L_2 = L_{2start}; T_L = T_{Lstart}, \text{ for } z = z_{max} \quad (19)$$

where  $z_{max}$  is the height of the absorber, m, the subscript start corresponds to the parameters at the entrance to the absorber.

### 3. Assessment of model parameters

The model parameters,  $p_1$ ,  $p_2$ ,  $p_3$  were calculated by comparison with the known experimental data (Field et al., 1962). The absorber is a column 9.1 m high, 0.15 m in diameter, filled with Rashig porcelain rings of size 0.012 m. The specific surface area for calculations is accepted  $a = 400 \text{ m}^{-1}$ . 50 experiments of single stream at a pressure of 2 MPa, were processed. The flow rate of gas saturated with water vapor varied in the range of 50–85 kmol/m<sup>2</sup>/h, the molar fraction of CO<sub>2</sub> at the inlet varied in the range from 15 to 30 %. The liquid flow rate was 300-900 kmol/m<sup>2</sup>/h, the carbonate mass fraction, equivalent K<sub>2</sub>CO<sub>3</sub> was 30 - 42 %, the conversion of K<sub>2</sub>CO<sub>3</sub> at the inlet varied from 10 to 40 %. The following estimates of the model parameters are obtained by the least squares method:  $[p_1 \ p_2 \ p_3] = [0.214 \ 0.0347 \ 0.513]$ ;

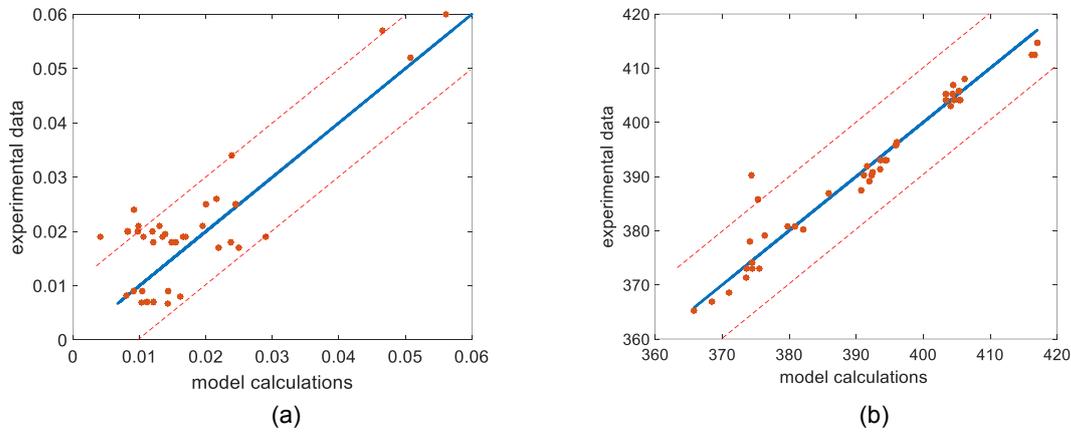


Figure 1: Calculation by model and experiment; (a), CO<sub>2</sub> mole fraction output, dashed lines correspond to the difference between the model and experiment equal to 0.01; (b), Fluid temperature at the bottom of the absorber, dashed lines correspond to the difference between the model and experiment equal to 10 K

The Figure 1 shows the results of the calculation according to the model and experimental data for the molar fraction of CO<sub>2</sub> in the purified gas, and bottom temperature of liquid. As you can see, there is a large spread for the concentration of carbon dioxide in the purified gas, the root mean square error is  $7 \times 10^{-3}$ .

### 4. Model adequacy check

The adequacy of the model was checked by comparing the calculations for the CO<sub>2</sub> concentration profile for the height of the absorber with 8 experiments from Table 16 of Field et al. (1962), not included in the sample, by which the model parameters were estimated. The standard error is 0.015. The parameters of two experiments with a typical error are presented in Table 1, the comparison results are in Figure 2.

Table 1: Experiment parameters (Field et al., 1962)

Parameter	Data 1	Data 2
Gas flow rate, kmol/m <sup>2</sup> /h	57	78
CO <sub>2</sub> mole fraction in gas	0.16	0.30
Liquid flow rate, kmol/m <sup>2</sup> /h	390	890
Carbonate concentration, equivalent K <sub>2</sub> CO <sub>3</sub>	0.355	0.365
Fraction conversion of the carbonate	0.4	0.33
Feed gas temperature, K	363	386
Liquid temperature, entering, top, K	363	386

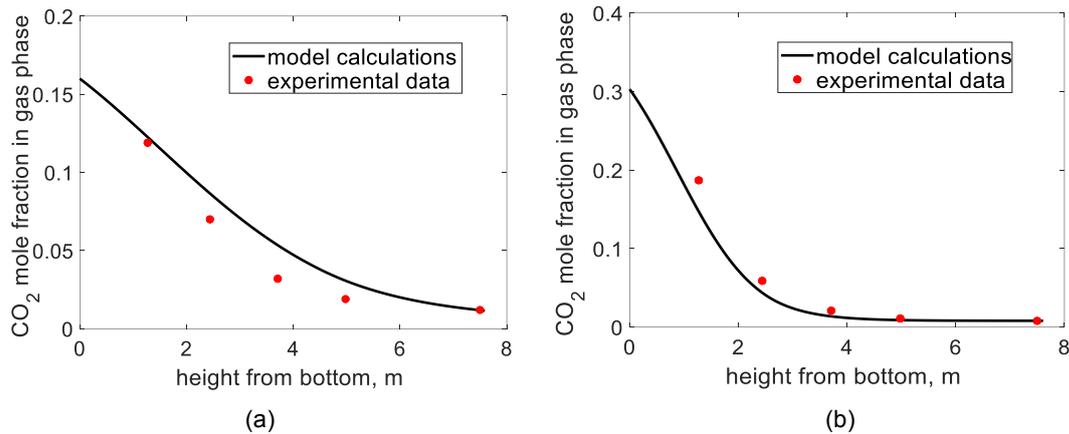


Figure 2: CO<sub>2</sub> concentration along the height of the absorber; (a) data 1; (b), data 2.

The model reproduces CO<sub>2</sub> concentration profiles and can be used to estimate the carbon dioxide yield from the physical characteristics of the process.

### 5. The influence of the physical characteristics of the process on the CO<sub>2</sub> output in the purified gas

Figure 3 shows the calculated dependences of the CO<sub>2</sub> yield on temperature at various gas and liquid flow rates. The parameters are presented in Table 2. For given liquid and gas flow rates, there is an optimal process temperature corresponding to the minimum CO<sub>2</sub> content in the purified gas. With increasing fluid flow rate, the optimum temperature increases. On the contrary, an increase in the gas flow rate leads to a decrease in the optimum temperature. Figure 4 shows the effect of K<sub>2</sub>CO<sub>3</sub> conversion on CO<sub>2</sub> output. The calculations were carried out at liquid and gas flow rates of 600 and 76 kmole/m<sup>2</sup>/h.

Table 2: Parameters of the calculations

Parameter	Value
CO <sub>2</sub> mole fraction in gas	0.2
Carbonate concentration, equivalent K <sub>2</sub> CO <sub>3</sub>	0.375
Fraction conversion of the carbonate	0.3
Feed gas temperature, K	384

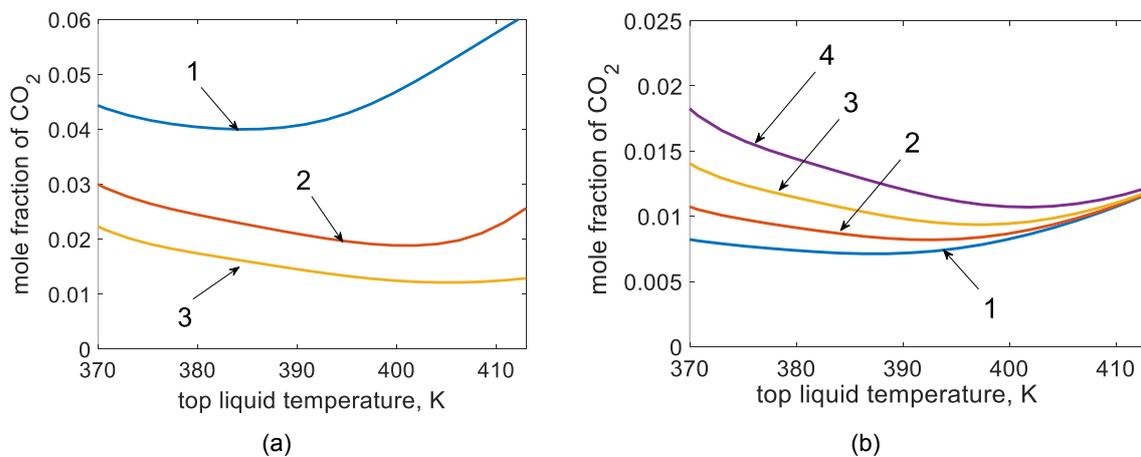


Figure 3: Model calculations. CO<sub>2</sub> output as a function of temperature; (a), at various flow rates of the liquid, 1 – 400, 2 – 500, 3 – 600 kmol/m<sup>2</sup>/h, flow rate of gas is 76 kmol/m<sup>2</sup>/h; (b), at various flow rates of the gas, 1 – 52, 2 – 58, 3 – 64, 4 – 70 kmol/m<sup>2</sup>/h, flow rate of liquid is 600 kmol/m<sup>2</sup>/h

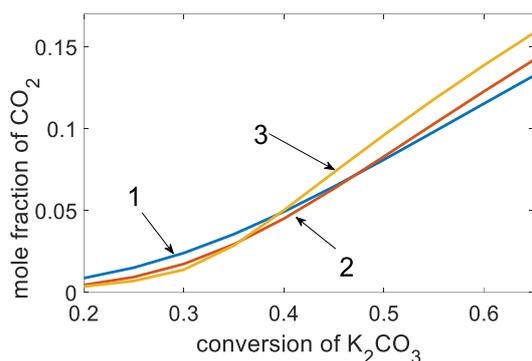


Figure 4: Model calculations.  $\text{CO}_2$  output as function of fraction conversion of the carbonate at various values of the liquid temperature, 1 – 380 K, 2 – 395 K, 3 – 410 K

## 6. Conclusions

The presented mathematical model of the process is consistent with the known experimental data in a wide range of parameters. The discrepancies between the model calculations and the known experimental data are due to both the approximate nature of the model and, possibly, experimental errors. Processing of more experimental data is required to refine the model. The study can be used as a theoretical basis for modeling the process of absorption of carbon dioxide by a solution of potassium carbonate with promoters.

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