MODELING HEAT AND MASS TRANSFER DURING GAS PURIFICATION IN THE SYNTHESIS OF AMMONIA*

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Mathematical models are proposed for the absorption of gases and regeneration of the solution in the synthesis of ammonia. The validity of the models is checked experimentally.

In modern systems designed for the production of ammonia, CO_2 is usually removed from the converter gas by using hot potash solutions activated with diethanolamine (DEA) in packed columns (Benfield process). This method of purification is based on the high absorption capacity of the solution and the high rates of absorption and desorption at elevated temperature. Under such conditions, absorption and regeneration of the solution can be realized at nearly the same temperatures. The absorpton process occurs at elevated pressure (22-25 bar), while regeneration of the solution occurs at a pressure close to atmospheric (1.1-1.3 bar). Figure 1 presents a diagram of the process by which the converter gas is purified of CO_2. The potash solution leaving the bottom part of the absorber is choked to a pressure close to atmospheric. The solution begins to undergo adiabatic expansion, and its temperature decreases due to evaporation of the absorbent and partial desorption of CO_2. Then the two-phase mixture is directed into the top part of the regenerator, where the CO_2 is desorbed by steam.

A mathematical model of the gas purification process is needed to efficiently design and optimize it. We have proposed models of an absorption column (absorber), a desorption column (regenerator), and the process of adiabatic expansion of the solution (expander). The models were checked experimentally using the example of gas purification in the commercial Benfield process.

Physicochemical Principles of the Gas Purification Process. The following reactions take place in the absorption (desorption) of CO_2 by aqueous solutions of potassium carbonates (potash) activated with DEA [1, 2]

$$CO_{2(g)} \rightleftharpoons CO_{2(L)}, \tag{1}$$

$$CO_{2(L)} + H_2O \rightleftharpoons H_2CO_3, \tag{2}$$

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-, \tag{3}$$

$$H_2O \rightleftharpoons H^+ + OH^-, \tag{4}$$

$$CO_{2(L)} + OH^- \rightleftharpoons HCO_3^-, \tag{5}$$

$$CO_{2(L)} + RR'NH \rightleftharpoons RR'NCOO^- + H^+, \tag{6}$$

$$RR'NH + H^+ \rightleftharpoons RR'NH_2^+, \tag{7}$$

$$RR'NCOO^- + H_2O \rightleftharpoons RR'NH + HCO_3^-. \tag{8}$$

The overall reaction is:

$$K_2CO_3 + CO_2 + H_2O \underset{\text{desorption}}{\overset{\text{absorption}}{\rightleftharpoons}} 2\,KHCO_3. \tag{9}$$

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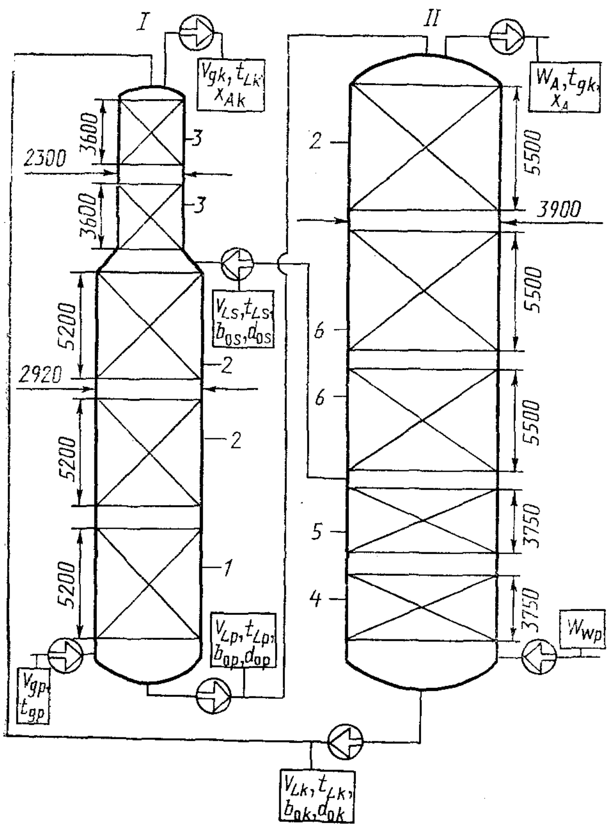

Fig. 1. Diagram of the gas purification process: I) absorber; II) regenerator; 1) Pall 50 column; 2) Pall 35 column; 3) Pall 25 column; 4) Bialetskii 35 column; 5) Intalox 1"; 6) Intalox 1.5".

It can be seen that CO_2 reacts simultaneously with three components, i.e., water, OH^- ions, and amine.

Under the conditions of the commercial process being examined, the overall reaction undergone by CO_2 is a rapid reversible reaction of the pseudo-first order. Meanwhile, chemical equilibrium is established in most of the fluid ($c_0 = c_r$) and the concentration of unreacted dissolved gas remains nearly constant along the diffusion path ($c_0 = c_r$ - const) [1, 2]. The rate of the overall reaction is expressed as

$$r = \{k_{H_2O} + k_{OH^-}[OH^-] + k_{Am}[Am]\}(c_A - c_{Ar}) = k_1(c_A - c_{Ar}), \tag{10}$$

while the absorption rate is equal to [2]:

$$\bar{R} = (x_A P - P_{Ar}) \frac{H\sqrt{Dk_1 + k_L^2}}{1 + (HRT/k_g)\sqrt{Dk_1 + k_L^2}}. \tag{11}$$

Mathematical Model of the Absorption Column. The absorption process, accompanied by a chemical reaction of the type

$$A + \beta B \rightleftharpoons \delta D, \tag{12}$$

occurs in a packed column. For a rapid pseudo-first-order reaction, when $c_0 = c_r$ = const, the balance equations can be represented in the form [1]

$$\beta\bar{R}(c_i, c_r, b_0, d_0)\, a\, dh = -\beta d(G_{0m} x_A) = (L_0/\rho_L)\, d(b_0). \tag{13}$$

For a dilute gas system [2]

$$d(G_{0m} x_A) \cong G_{0m}/(1 - x_A)\, dx_A = (L_0/\rho_L)\, d(b_0). \tag{14}$$

Here the quantity of absorbed CO_2 is equal to

$$\frac{dx_A}{dh} = -\frac{(1-x_A)}{G_{0m}}\overline{R}a. \tag{15}$$

In the heat balance, we account for heat exchange between the gas and the liquid, evaporation of the absorbent, the thermal effect of dissolution, the reactions of the absorbed gas, and heat losses to the environment.

Heat Exchange between Phases. Ignoring the thermal resistance of the liquid [3] and using the method of heat-transfer units, we obtain

$$dN_t = \alpha_t\, a\,(T_g - T_L)\,dh. \tag{16}$$

From the heat balance

$$dN_t = (G_{0m}C_pT_g) = G_{0m}C_p dT. \tag{17}$$

As a result,

$$\frac{dT_g}{dh} = \frac{\alpha_t\, a\,(T_g - T_L)}{C_p\, G_{0m}}. \tag{18}$$

The heat-transfer coefficient α_t can be determined from an analogy between heat transfer and mass transfer in the form

$$\frac{\mathrm{Nu}_g}{\mathrm{Sh}_g} = \frac{A'\,\mathrm{Re}_g^{B'}\,\mathrm{Pr}_g^{C'}}{A'\,\mathrm{Re}_g^{B'}\,\mathrm{Sc}_g^{C'}} = (\mathrm{Pr}_g/\mathrm{Sc}_g)^{C'}. \tag{19}$$

Taking C' = 0.33, we can reduce Eq. (18) to the form

$$\frac{dT_g}{dh} = \frac{k_g\, a}{G_{0m}}\left(\frac{\lambda_g M_g}{C_p D_g}\right)^{0,66}\rho_g^{0,33}(T_g - T_L). \tag{20}$$

Evaporation of the Absorbent (Water). In this case, if we ignore diffusional resistance in the liquid phase [3] and use the method of heat-transfer units, we obtain

$$dN = k_g'\, a\,(x_w P - p_{wr})\,dh. \tag{21}$$

From the mass balance

$$dN = d(G_{0m}x_w) = G_{0m}/(1 - x_w)\,dx_w. \tag{22}$$

As a result,

$$\frac{dx_w}{dh} = \frac{k_g'\, a\,(1 - x_w)}{G_{0m}}\,(x_w P - p_{wr}). \tag{23}$$

The thermal effect of evaporation (or condensation) is equal to the product of the heat of vaporization and the amount of evaporated absorbent. The thermal effects of dissolution and the reaction of the absorbed gas are equal to the product of the heats of solution and reaction and the quantity of absorbed gas.

Under these conditions, the heat-balance equation can be represented in the form

$$\frac{dT_L}{dh} = \frac{G_{0m}}{L_0 c_L}\left(-C_p\frac{dT_g}{dh} + q_w\frac{dx_w}{dh} + q_A\frac{dx_A}{dh}\right) + \frac{q_s}{L_0\, c_L}. \tag{24}$$

Calculation of heat and mass transfer along the height of the packing reduces to the simultaneous solution of the following differential equations: Eqs. (15) and (23), describing the profiles of concentration of the absorbed gas x_A and the vapor of the absorbent x_w in the gas phase; balance equations (20) and (24), describing the profiles of the temperatures of the gas T_g and liquid T_L; the equations

$$\frac{d(b_0)}{dh} = \frac{\rho_L}{L_0}\overline{R}a, \tag{25}$$

$$\frac{d(d_0)}{dh} = -2\frac{d(b_0)}{dh}, \tag{26}$$

describing the profiles of the concentration of the substrate b_0 (potassium carbonate) and the reaction product d_0 (potassium bicarbonate) in the liquid phase; the balance equations

$$\frac{dG_0}{dh} = 44\, G_{0m} \frac{dx_A}{dh} + 18\, G_{0m} \frac{dx_w}{dh}, \tag{27}$$

$$\frac{dL_0}{dh} = \frac{dG_0}{dh}, \tag{28}$$

describing the profiles of the mass velocities of the gas G_0 and liquid L_0.

The method used to calculate the properties of the gas and liquid, the equilibrium (Henry) coefficient, and the diffusion and mass-transfer coefficients in the gas and liquid phases was first proposed in [2].

The equilibrium pressures of CO_2 (p_{Ar}) and H_2O (p_{wr}) above the potash solutions, needed to accurately calculate the rate of absorption of CO_2 and rate of evaporation of water, were determined from equations of the type

$$p_{Ar} = f(b_0,\ d_0,\ T),\ p_{wr} = f'(b_0,\ d_0,\ T), \tag{29}$$

which generalize the results of commercial trials [4, 5].

We developed a program for performing numerical calculations by the Runge–Kutta–Merson method and we conducted an empirical check of the model. The results of the calculations and the commercial trials are shown in Table 1. We obtained good agreement between the calculated and experimental values of the degree of absorption η and the temperature of the liquid in the top part of the absorber (the calculations were begun with the bottom part of the absorber).

Mathematical Model of Adiabatic Expansion of the Solution. When the solution is fed from the bottom of the absorber to the regenerator, a substantial reduction in pressure causes the solution to expand adiabatically in the pipe taking the liquid from the absorber and in the top part of the regenerator. The temperature of the solution begins to decrease, the absorbent begins to evaporate, and the CO_2 begins to undergo partial desorption. The result is the formation of a two-phase mixture (Fig. 2).

The balance equations can be represented in the following form:

the overall material balance

$$V_{Lp}\rho_{Lp} = V_{Lz}\rho_{Lz} + V_{gz}M_g, \tag{30}$$

the material balance of potassium

$$V_{Lp}\left(b_{0p} + \frac{d_{0p}}{2}\right) = V_{Lz}\left(b_{0z} + \frac{d_{0z}}{2}\right), \tag{31}$$

the material balance of carbon

$$V_{Lp}(b_{0p} + d_{0p}) = V_{Lz}(b_{0z} + d_{0z}) + V_{gz}x_{Az}, \tag{32}$$

TABLE 1. Results of Calculations and Experiments

Absorber				experiment			
Regenerator		calculations		Regenerator		calculations	
η, %	t_{Lk}, °C	η, %	t_{Lk}, °C	t_{gk}, °C	W_A, kmole/h	t_{gk}, °C	W_A, kmole/h
98,98	99	98,33	100	102	475	100	482
98,59	113	98,54	114	102	494	103	487
98,98	101	98,84	101	102	482	101	488
98,63	112	98,13	114	101	480	100	490
99,24	102	99,39	102	103	478	103	485
99,13	113	99,13	115	104	481	104	490
99,21	98	99,26	98	101	350	99	345
98,81	113	98,91	113	101	358	103	347
99,21	99	99,36	98	101	355	101	351
99,26	99	99,36	99	100	338	101	342

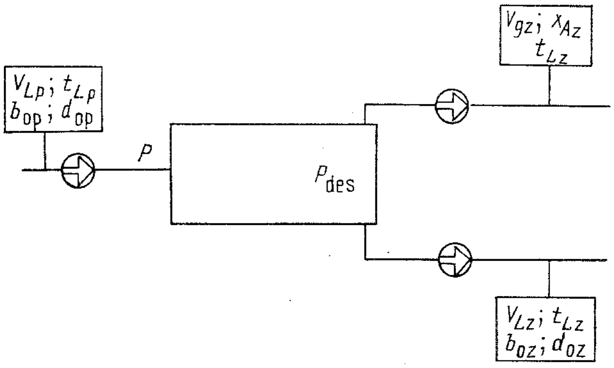

Fig. 2. Diagram of the adiabatic expansion of the solution.

the heat balance

$$V_{Lp}\rho_{Lp}c_{Lp}t_{Lp} = V_{Lz}\rho_{Lz}c_{Lz}t_{Lz} + q_w V_{gz}x_{wz} + q_A V_{gz}x_{Az} + V_{gz}C_{pz}t_{Lz}\,, \tag{33}$$

where

$$x_{Az} = \frac{p_{Az}}{p_{des}}\,,\quad x_{wz} = \frac{p_{wz}}{p_{des}}\,. \tag{34}$$

It was shown in [6, 7] that the ability of water to rapidly evaporate nearly guarantees satisfaction of the equality $p_{wz} = p_{wr}$. On the other hand, the partial pressure of CO_2 is considerably less than the equilibrium value. Also,

$$p_{Az} = k_A p_{Ar}\,. \tag{35}$$

The coefficient k_A was determined from special tests [2, 6]. (Under the conditions being examined here, $k_A = 0.4$-0.5.)

Simultaneously solving Eqs. (30)-(35) and (29), we find the temperature, complete composition, and quantity of the gas and liquid after adiabatic expansion of the solution.

Mathematical Model of the Desorption Column. Here, the potash solution is regenerated, i.e., CO_2 is desorbed. Only the sign of the process changes. The rate of desorption, accompanied by a chemical reaction, can be determined from the same equation as absorption by changing the sign of the driving force of the process [1]. In Eq. (11), in place of $(x_AP - p_{Ar})$ we need to put $(p_{Ar} - x_Ap_{des})$. The gas phase, consisting of two components (water vapor and carbon dioxide), cannot be regarded as a dilute system.

The balance equation for CO_2 is

$$dN_A = \bar{R}adh = d(G_{0m}x_A) = x_A\,dG_{0m} + G_{0m}dx_A\,, \tag{36}$$

from which

$$\frac{dx_A}{dh}\;\frac{\bar{R}a}{G_{0m}} - \frac{x_A}{G_{0m}}\,\frac{dG_{0m}}{dh}\,. \tag{37}$$

For a two-component system

$$G_{0m} = N_A + N_w. \tag{38}$$

Then

$$\frac{dG_{\upsilon m}}{dh} = \frac{dN_A}{dh} + \frac{dN_w}{dh} = \bar{R}a + k_g' a\,(x_w P_{des} - p_{wr}). \tag{39}$$

Since $x_A + x_W = 1$, the concentration profile for the water vapor can be found from the equation

$$\frac{dx_w}{dh} = -\frac{dx_A}{dh}\,. \tag{40}$$

The profiles of the mass velocities of the gas and liquid over the height of the packing are given by the equations:

$$\frac{dG_0}{dh} = \frac{d}{dh}(44\,x_A\,G_{0m} + 18\,x_w\,G_{0m}) = 44\,G_{0m}\frac{dx_A}{dh} + 18\,G_{0m}\frac{dx_w}{dh} + (44\,x_A + 18\,x_w)\frac{dx_{0m}}{dh}, \tag{41}$$

$$\frac{dL_0}{dh} = \frac{dG_0}{dh}. \tag{42}$$

The concentrations of the products and substrates of the reaction are found from the equations

$$\frac{d(b_0)}{dh} = -\frac{\rho_L}{L_0}\bar{R}\,a, \tag{43}$$

$$\frac{d(d_0)}{dh} = -2\,\frac{d(b_0)}{dh}. \tag{44}$$

As in the case of adiabatic expansion of the solution, due to the rapidity of the process, we took the partial pressure of the water vapor to be equal to the equilibrium value. Ignoring the thermal resistance of the liquid, we determine the temperature of the gas and liquid from Eq. (29) in the form

$$T_g = T_L = 5010.75/\left[16.0545 + 0.2549\ln\alpha - 1.06302\,\alpha + 0.84335\ln w - 3.74683\,w - \ln\left(\frac{P_{\text{des}}\,x_w}{\alpha + 0.65}\right)\right], \tag{45}$$

where

$$\alpha = \frac{d_0}{2b_0 + d_0}. \tag{46}$$

Solving Eqs. (36)-(46), we obtain the profiles of the temperatures, concentrations, and mass velocities of the gas and liquid in the regenerator over the height of the packing.

In the top part of the regenerator, the gas phase mixes with the liquid phase after adiabatic expansion of the solution and the gas is discharged into the atmosphere.

Thus, using models of adiabatic expansion and a desorption column, we calculated the temperature and composition of the gas at the outlet of the regenerator. It can be seen from the table that good agreement is obtained between the theoretical and experimental values found for the temperature and quantity of desorbed CO_2.

NOTATION

a, phase contact surface referred to a unit volume of the packing (m^2/m^3); b_0, concentration of carbonate ($kmole/m^3$); c_A, concentration of CO_2 ($kmole/m^3$); c_L, specific heat of the liquid [$kJ/(kg\cdot K)$]; C_p, molar heat of the gas [$kJ/(kmole\cdot K)$]; d_0, concentration of dicarbonate ($kmole/m^3$); D, diffusion coefficient (m^2/sec); G_0, mass velocity of the gas (kg/m^2); G_{0m}, molar velocity of the gas [$kmole/(m^2\cdot sec)$]; h, height of packing (m); H, Henry's constant [$kmole/(m^2\cdot sec\cdot bar)$]; k_1, rate constant of reaction of pseudo-first order (sec^{-1}); k_{Am}, rate constant of reaction (6) [$m^2(kmole\cdot sec)$]; k_{H_2O}, rate constant of reaction (2) (sec^{-1}); k_{OH}, rate constant of reaction (5) [$m^3/(kmole\cdot sec)$]; L_0, mass velocity of liquid [$kg/(m^2\cdot sec)$]; N, diffusion flux referred to a unit of the phase boundary [$kmole/(m^2\cdot sec)$]; Nu, Nusselt number; p, partial pressure (bar); P, total pressure (bar); q_A, heat of solution and reaction (kJ/kmole); q_s, heat losses to the environment [$kJ/(m^2\cdot sec)$]; q_w, heat of vaporization of the absorber (kJ/kmole); R, gas constant [$kJ/(kmole\cdot K)$]; $\bar{R}$, absorption rate referred to a unit of the cross section [$kmole/(m^2\cdot sec)$]; Re, Reynolds number; Sc, Schmidt number; Sh, Sherwood number; t, T, temperature (°C; K); W, mass fraction of carbonates; V, volumetric flow rate (m^3/sec); W, molar flow rate (kmole/h); x, molar fraction; α_t, heat-transfer coefficient [$kJ/(m^2\cdot sec\cdot K)$]; ρ, density (kg/m^3); $\eta = (x_{Ap} - x_{Ak})/x_{Ap}$, degree of absorption. Indices: A, CO_2; des, desorption; g, gas; k, top of column; L, liquid; p, bottom of column; r, equilibrium; s, middle of column; w, absorbent (water); z, expander.

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