

Modelling of a Gas-Absorption Packed Column for Carbon Dioxide-Sodium Hydroxide System

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Abstract

This paper present a research work on the modeling of a gas absorption packed column with the aim formulating a mathematical model and simulation of the model using a computer software to obtain the rate of absorption and the amount of absorbed carbon dioxide CO₂ into dilute sodium hydroxide NaOH. Arm field gas absorption column titration techniques were used for the analysis. The total concentration of carbonate and hence the amount of carbon dioxide absorbed was determined using gravimetric methods. The comparison between the obtained experimental and simulated results shows that the formulated model is a good representation of the system. A program was written in Q-Basic for simulation of any gas absorption packed column, the model and computer program could therefore be used to determining the condition in a counter-current continuous column at any given time, for any chemically reacting absorption system.

Keywords: *Packed column, modeling, simulation, gas-absorption, Q-Basic, carbon dioxide - sodium hydroxide system.*

Introduction

Chemical reactor design is based on the modeling of reactors and of the reactions that take place in them (Levenspiel 1972). A mathematical model is a simplified image of the processes that take place in a reactor. It retains the most essential properties of the actual process and presents them in mathematical form. Depending on the objective sought, a mathematical model may involve a varying number of properties of the prototype, and so it may be wide or narrow. Mathematical modeling is so important that it is now being used in computer simulations (Levenspiel 1972).

Simulation represents the application of modeling techniques to real systems, thus enabling information on plant characteristics to be gained without either constructing or operating the full scale plant or the system under consideration (Levenspiel 1972). Simulation methods in chemical reactor designs are of two types, digital and analogue. Digital simulation involves the use of codes and

programs are more in use since they can be implemented on modern computers with exceptional speed (Levenspiel 1972).

Most reactions utilized in the chemical process industries involve substances, which exist in different phases. There may be two-phase (binary) and three-phase (tertiary) systems (Coulson 1996). For all the differences between them, they have one thing in common. Before a chemical reaction can take place, the reactants must be transported from the bulk of the stream and carry one phase to the inter-phase boundary or into bulk of the other phase.

Gas liquid absorption is a heterogeneous process, which involves the transfer of a soluble component of a gas phase into a relatively non-volatile liquid absorbent (Franks 1967). Gas liquid absorption could be employed in purification of waste gases (Coulson 1996).

In this work, a mathematical model was developed and simulated for a gas-liquid absorption packed column operating under a continuous mode for the absorption of carbon dioxide in to dilute caustic soda via

determination of the overall performance of the absorption column.

Description and Operation of the Gas Absorption Column

Gas absorption is usually carried out in vertical counter current packed column 75mm in diameter in which there are two lengths of rancing. The liquid solvent is fed at the top of the column and is distributed over the surface of the packing either by nozzle or distribution plates. Pressure tapping is provided at the base, center and top of the column to determine pressure drops across the column. Sampling points are also provided for the gas at the same three points. The liquid outlet stream and feed solution are also equipped with sampling point. Suitable manometer measurement is included. Water/solvent is taken from a sump tank, and pumped to the column via a calibrated flow meter. Gas is taken from a pressure cylinder through a calibrated flow meter, and mixed with air, supplied and monitored from a small compressor in a pre-determined (but variable) mixed ration. The mixture is fed to the base of the tower, in which a liquid seal is provided. The effluent gas leaves the top of the column and is intended to be exhausted to atmosphere outside the laboratory building. The apparatus is designed to absorb CO₂ / Air mixture into an aqueous solution flowing down the column. Gas analysis is provided for this system (see Fig. 1).

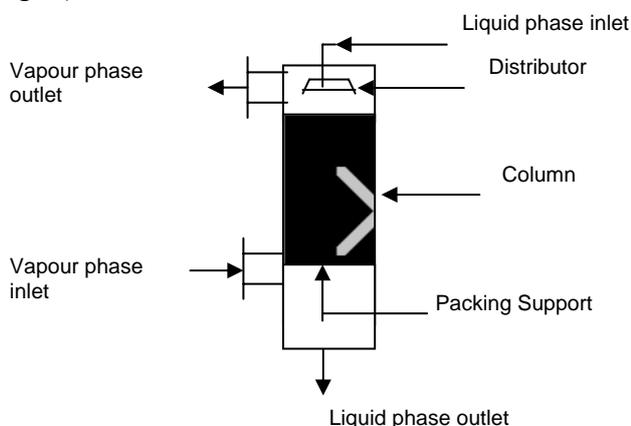


Fig. 1. Gas Absorption Column.

Application of Mass Transfer Theories

The analysis of the process of absorption so far given is based on the two-film theory of Whitman (1923). It is supposed that the two films have negligible capacity, but offer all the resistance to mass transfer, and thus the flow is considered to be laminar and parallel to the surface. An alternative theory was proposed by Higbie (1935) and later extended by Danckwerts and Kennedy (1954) which gave mass transfer rate (N_A) to be directly proportional to the concentration difference ($C_{AI} - C_{AL}$). However, Higbie–Danckwerts also used $N_A \propto VD_L$. Whereas $N_A \propto VD_L$ in the two-film theory, Danckwerts applied this theory to the problem of absorption coupled with chemical reaction but although in this case the three proposals give somewhat different results, it has not been possible to distinguish between them. The application of penetration theory to the interpretation of experimental results obtained in wetted-wall columns has been studied by Lynn *et al.* (1955).

CO₂-NaOH Reaction System

The reaction is the absorption of carbon-dioxide into dilute caustic soda termed as chemisorptions and is similar to the basic gas liquid reactions widely used in chemical process industries as auxiliary steps in the purification of gas mixtures:



Mathematical Modeling for Arm Field Gas Absorption Column

The process of interest is the absorption of carbon dioxide into dilute solution of caustic soda using the Arm field gas absorption column (packed with rancing rings). For proper understanding of the behavior of the system, prior knowledge of rate of reaction mass and energy balances together with simple chemical reaction kinetics are required.

The following assumptions are taken into consideration in developed/developing model for gas absorption packed column and in the analysis of the predicted result of the model:

1. Absorption process is carried out in a series of contacts, with the occurrence of unidirectional mass transfer and occurs counter-currently using diluted absorbent.
2. The column operates at steady state conditions, hence there are negligible heat effects in the column and the absorption process is accompanied by (pseudo-first order reaction).
3. There exist constant molal flow rates due to the occurrence of perfect mixing.

Derivation of Mathematical Model for Arm Field Gas Absorption Column Overall Material Balance

Mathematical analysis of a process is always based on the material balance of the process drawn up for one of the components of the reaction mixture and can be written as differential equations for the elementary volume. The material balance equation for the main component contains the following terms:

$$G_t = G_d + G_r + G_a, \tag{2}$$

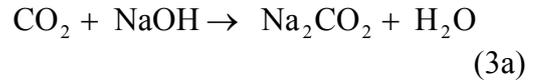
where G_t is the amount of the component fed to the elementary volume per unit time; G_d is the amount of the component out from the elementary volume per unit time; G_r is the rate of consumption of the component in the chemical reaction in the elementary volume; and G_a is the rate of accumulation of the component in the elementary volume.

This can be written for the whole reactor if there is uniform distribution of materials over the reactor volume.

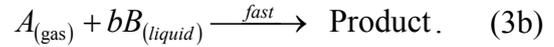
Differential Material Balance

The material balance of 'A' (CO₂) and 'B' (NaOH) is obtained by noting that the two reactants, A alone is present in the main body of gas and B alone is present in the main liquid. Secondly, for each mole of 'A' reacted, 'b'

moles of 'B' are consumed. In this case, for each mole of CO₂ reacted, 2 moles of NaOH are consumed,



given by $A + bB \rightarrow \text{Products}$, $b = 2$. Referring to the diagram below (see Fig. 2),



However material balance about the end of tower gives composition at any point in tower.

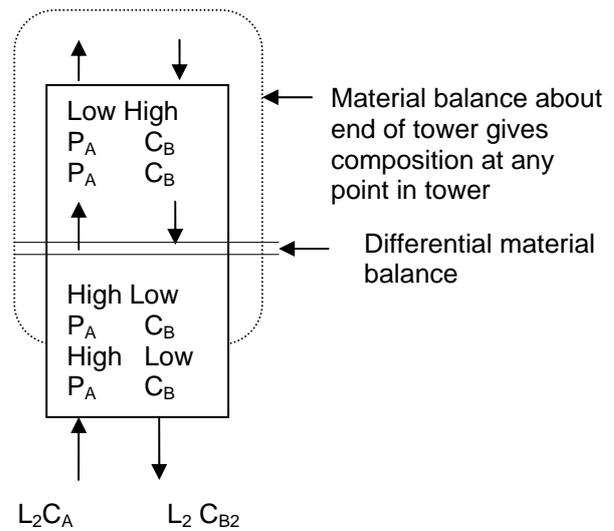


Fig. 2. Material balance.

The differential material balance for the counter current flow is as shown below:

$$[A' \text{ lost by gas}] = \frac{1}{b} [B' \text{ lost by liquid}] \tag{4}$$

or

$$\begin{aligned} G dY_A &= \frac{-L}{b} dX_B = -L d \left[\frac{C_B}{C_U} \right] \\ &= d \left[\frac{G' P_A}{\pi} \right] = \frac{-1}{b} d \left[\frac{L' C_B}{C_T} \right] \end{aligned} \tag{5}$$

Compositions at any point in the tower are found in terms of the end conditions by integrating the material balance equation. Thus

$$\begin{aligned} G[Y_A - Y_{AI}] &= -L \frac{(X_B - X_{BI})}{b} \\ &= G \left[\frac{P_A}{P_U} - \frac{P_{AI}}{P_{UI}} \right] = -\frac{L}{b} \left[\frac{C_B}{C_U} - \frac{C_{BI}}{C_{UI}} \right] \\ &= \frac{G'' P_A}{\pi} - \frac{G'' P_{AI}}{\pi} \end{aligned}$$

$$= \frac{-I}{b} - \left[\frac{L'C_B}{C_T} - \frac{L'C_{BI}}{C_{TI}} \right] \quad (6)$$

The above expressions give the concentrations of reactants *A* and *B* in the phases throughout the tower,

$$P_U \approx \pi C_U \approx C_T \quad (7)$$

Equations 5 and 6 for differential material balance become

$$\frac{GDP_A}{bC_T} = -LdC_B, \quad (9)$$

and for point conditions,

$$G(P_A - P_{AI}) = \frac{-L}{bC_T} (C_B - C_{BI}). \quad (10)$$

Height of Tower Equation

The height to tower (column) is found by combining rate equation and material balance for a differential element of tower and is given by:

$$h = \gamma_A = \frac{1}{K_{Ag}} + \frac{HA}{\sqrt{ALKC_B}}, \quad (11)$$

rearranging and integrating, in terms of *A* and *B*.

Rate of absorption of a substance gas which diffuse into liquid film stagnant medium in which it has a limited solubility and with which undergoes an irreversible first order or pseudo first reaction is assumed to obey ideal diffusion law,

$$\frac{dQ}{dt} = -\frac{D\partial C}{\partial X}. \quad (12)$$

This holds for the diffusion of unreacted solute through the medium, and also that the mass of solvent per unit volume of the medium is virtually constant throughout.

Let C^* be the saturated concentration of the solute reigning at the surface ($X = 0$); C - concentration at a distance X below the surface; t - time; and k - velocity constant of the reaction between solute and medium.

Initial concentration of solute in the medium is uniformly equal to zero. Hence, rate at which the solute crosses unit area of any plane of constant X in the direction of increasing X is

$$\left(\frac{dQ}{dt} \right) = -\frac{D\partial C}{\partial X}. \quad (13)$$

Consider the element of volume of unit cross-sectional area between planes X and $X + dX$. The following changes in its content of solute occur in timidity:

$$\text{Diffusion (in)} = \frac{-D\partial C}{\partial X} dt, \quad (14)$$

$$\begin{aligned} &\text{Diffusion (out)} \\ &= \left\{ -Ddt \left(\frac{\partial C}{\partial X} + \frac{\partial^2 C}{\partial X^2} dX \right) \right\}, \quad (15) \end{aligned}$$

$$\text{Reacting} = -kcdt.dX, \quad (16)$$

$$\text{Net Increase} = \left[\frac{D\partial^2 C}{\partial X^2} - kc \right] dt.dX. \quad (17)$$

If increase in concentration is dc , the net increase above can be equated to dc/dx , giving

$$\frac{dc}{dt} = D \frac{\partial^2 C}{\partial x^2} - KC. \quad (18)$$

With the boundary conditions:

$$\begin{aligned} C &= C^*, x = 0, t > 0, \\ C &= 0, x > 0, t = 0, \\ C &= 0, x = \infty, t > 0, \end{aligned} \quad (19)$$

the solution to equation 18 is

$$\frac{C}{C^*} = \frac{1}{2} \exp\left(-X\sqrt{\frac{K}{D}}\right) \text{erfc} \quad (20)$$

where $\text{erfc} = 1 - \text{erf}z$,

$$z = 1 - \frac{2}{\sqrt{\pi}} \int_0^z \exp(-y^2) dy \quad (21)$$

Differentiating Eq. (21),

$$\begin{aligned} &\frac{\partial c}{\partial x} \left(\frac{\partial c}{\partial x} \right)_{x=0} \\ &= -C^* \sqrt{\frac{D}{K}} \left[\text{erf} \sqrt{Kt} + \frac{e^{-kt}}{\sqrt{\pi kt}} \right]. \quad (22) \end{aligned}$$

The rate of absorption dQ/dt per unit area of surface becomes

$$\begin{aligned} &\frac{dQ}{dt} = -D \left(\frac{\partial c}{\partial x} \right)_{x=0} \\ &= C^* \sqrt{\frac{D}{K}} \left[\text{erf} \sqrt{Kt} + \frac{e^{-kt}}{\sqrt{\pi kt}} \right]. \quad (22a) \end{aligned}$$

Quantity Q absorbed in time ' t ' is

$$Q = C^* \sqrt{\frac{D}{K}} \left[\left(Kt + \frac{1}{2} \right) \text{erf} \sqrt{Kt} + \sqrt{\frac{Kt}{\pi}} e^{-kt} \right],$$

$$(22b)$$

when Kt is sufficiently large, $\text{erf} = \sqrt{Kt} \approx 1$,

$$\frac{C}{C^*} \approx \exp\left(-x\sqrt{\frac{K}{D}}\right). \quad (23)$$

Then

$$\frac{\partial Q}{\partial x} dQ \approx C^* \sqrt{DK} \quad (24)$$

and

$$Q = C^* \sqrt{\frac{D}{K}} \left(Kt + \frac{1}{2}\right). \quad (25)$$

Determination of the Absorption Acceleration Factor in the Case of a Chemical Reaction ‘ ε ’

If $aA_{(g)} + bB_{(l)} \rightarrow \text{Product}$, the true rate equation is

$$\omega_{rA} = KC_A C_B. \quad (26)$$

This could also be written as

$$\omega_{rA} = K^1 C_A, \quad (27)$$

where

$$K^1 = KC_B^n. \quad (28)$$

The concentration of reactant A in the boundary film decreases not only due to diffusion, but also because it is used up in the reaction. This leads to an increased concentration gradient of the reactant at the interface and the numerical value of the slope of the tangent of the $C_A Z$ curve at point M equal to $\text{grad } C_A$, increases. As a result, the individual coefficient of mass transfer from the gas to the liquid phase is increased,

$$W_A = D \text{ grad } C_A. \quad (29)$$

This can be written as

$$W_A = \beta_i \left\{ C_{Ab} - C_{Al} \text{Cosh}\left(M^{\frac{1}{2}}\right) M^{\frac{1}{2}} \tanh\left(M^{\frac{1}{2}}\right) \right\}. \quad (30)$$

where

$$\beta_i = \frac{D}{\delta} = \varepsilon, \quad (31)$$

which describes absorption accompanied by a chemical reaction and it differs from equation

$$W_A = \beta_i (C_A - C_{AL}), \quad (32)$$

which describes physical absorption

$$W_A = \beta_i (C_A - C_{AL}). \quad (33)$$

When a fast chemical reaction takes place in the film and $C_{AL} = 0$, Eq. 30 takes a simpler form:

$$\omega A = \beta C_{AB} \left(\frac{M^{\frac{1}{2}}}{\tanh M^{\frac{1}{2}}} \right) \quad (34)$$

The absorption accelerator factor ‘ ε ’ may be found by equating Eqs. (34) and (31) at $C_{AL} = 0$. ε is the factor in the equation describing absorption accompanied by a chemical reaction physical absorption equation. At $C_{AL} = 0$,

$$\varepsilon = \frac{\beta C_{Ab}}{\beta_1 C_{Ab}} M^{\frac{1}{2}} \tanh\left(M^{\frac{1}{2}}\right) = M^{\frac{1}{2}} \tanh\left(M^{\frac{1}{2}}\right), \quad (35)$$

or at $M^{1/2} \gg 1$ (because then $\tanh M^{1/2}$ tends to unity),

$$\varepsilon = M^{\frac{1}{2}} = \left(\frac{DK}{B^2 L} \right)^{\frac{1}{2}} = \frac{(KD)^{\frac{1}{2}}}{\beta_2 L}. \quad (36)$$

Thus, it is seen that an increase in the reaction rate constant K leads to greater absorption acceleration factors ε .

Determination of the Rate of Absorption of CO₂ into NaOH

Methodology

This experiment is aimed at determining the rate of absorption of carbon dioxide into caustic soda solutions (NaOH) through analysis of liquid solution flowing down the absorption column and the effect of time on the absorption rates.

Procedures (Equipment setting up)

1. 7½ L of IM solution of caustic soda was prepared and poured in 30litres of water to make 37.5litres of 0.2M solution of caustic soda, then poured into the reservoir tank at the base of the column.
2. The gas flow control valves C_5 and C_3 were closed, the liquid pump started and the flow of caustic soda through the column was adjusted to approximately 3litres/min on flow meter F_1 by adjusting control valve C_1 .
3. The compressor was started and valve C_2 adjusted to give an air flow of

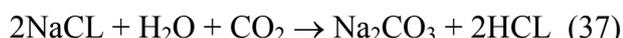
approximately 30litres/minute on the flow meter F_2 .

4. The pressure regulating valve on the carbon-dioxide cylinder was carefully opened and the valve C_3 adjusted to give a flow of 3litres/min on flow meter F_3 .
5. After 25 minutes of steady operation, samples were taken at the 30th minute interval simultaneously from S_4 and S_5 and the result were recorded.

Determination of Amount of HCl Needed To Neutralize All Hydroxide and Convert Carbonate To Bicarbonate

Procedure

1. 250ml of liquid sample was taken from the absorption column liquid outlet or sump tank into a conical flask and two 50ml portions were pipette into two separate conical flasks: flask 1 and flask 2 respectively.
2. A drop of phenolphthalein indicator was added to content in flask 1 and titrated with standard hydrochloric acid until the pink colour disappeared and the volume of acid added t, noted; hence T_1 is that amount of HCL needed to neutralize all hydroxide and converted carbonate to bicarbonate. A drop of methyl orange indicator was added to flask 1 again and 1st titration and still titrated with standard HCL until the endpoint T_2 and hence the total acid added was noted, hence the acid added denoted the neutralization of all bicarbonates ($T_2 - T_1$).
3. 10% more than the value of ($T_2 - T_1$) of Barium chloride solution was added to flask 2 and the contents shook well. This precipitated out all the original carbonate in the sample as Barium carbonate. Two drops of phenolphthalein solution were then added and titration carried out against the standard acid solution to the end point, hence the amount of acid added to T_2 was noted representing that needed to neutralize only the original caustic soda ($T_2 - T_1$), this represent the difference between the total acid required for hydroxide alone. Overall Reaction:



Determination of Carbon dioxide Remove Determination of Overall Mass Transfer Coefficient (K_{og})

This experiment is aimed at determining the overall Mass transfer coefficient (K_{og}).

Procedure

The experiment was conducted as was for experiment (2), except that the liquid analysis was omitted as the gas analysis alone could determine the rate of absorption.

1. The water reservoir tank was three – quarter full of 0.2M caustic soda solution.
2. The water pump was switched on and C_1 set to give a flow rate of 3litres/minutes down the column.
3. After 30 seconds, C_1 was close and the pump switched off, the column was drained for 5 minutes.
4. Air pressure differential across the wet column as a function of air flow rate was measured.
5. Air pressure across the column as a function of the air flow rate for different water flow rates up to 6.5litre/minutes were measured and the appearance of the column at each setting was noted.

Results

The results of various experiments carried out to test the model are presented in Tables 1 to 4. However, the following are kept constant throughout the experiment:

- Volume of solution in system: 37.5litres;
- Flow of solution (F_1): 0.05litres/sec;
- Air temperature: 28^oC.

Table 1. Analysis of Liquid Sample to Sump tank S_4

Time from start (mins)	T_1 /ml	T_2 /ml	T_3 /ml	$T_2 - T_1$ /ml	$T_2 - T_3$ /ml
0	38.6	40.0	37.8	1.4	2.2
30	25.5	42.2	9.8	16.5	32.4
60	16.5	41.1	2.6	24.6	38.5
90	19.8	47.4	0.8	38.6	46.6

Table 2. Analysis of Liquid Sample from Sump Tank (Inlet) S₄

TIME	T ₁ /ml	T ₂ /ml	T ₃ /ml	C _C	C _N
0.0	31.10	42.30	20.6	0.08	0.04
30	18.90	41.50	4.85	0.02	0.07
60	15.00	49.50	1.40	0.01	10.9
90	9.50	49.00	0.04	0.02	0.10

Table 3. Experimental Result of CO₂ Absorbed (Gmols/sec)

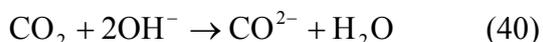
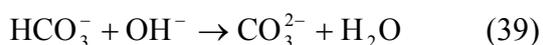
t/sec x 10 ³	NaOH concentration gram. mole/sec x 10	Quantity of CO ₂ absorbed gram mole/sec	$\sqrt{t \text{ sec}}^{-\frac{1}{2}}$
0.00	1.60	0.00197	0.00
1.80	0.40	2.265	42.43
3.60	0.10	2.725	60.00
5.40	0.00	3.33	73.50

Table 4. Results from Simulation

t/sec x 10 ³	Quantity of CO ₂ absorbed g/mole/sec	$\sqrt{t \text{ sec}}^{-\frac{1}{2}}$
0.00	0.00	0.00
1.80	1.555	42.43
3.60	2.916	60.00
5.40	4.374	73.50

Discussion of Results

The analysis of the absorption of CO₂ into NaOH solution, revealed that Diffusion of CO₂ into a solution containing almost uniform concentration of OH ions follow the following path.



The reactions of Eqs. (38) and (40) are first order with respect to CO₂ and OH and

having the same velocity constant $K = K^1$ (OH) less than that of Eq. (39).

The predictive model equation for the quantity of absorbed CO₂ in a given time (*t*) by diffusion accompanied by chemical reaction is given by

$$Q = C^* \sqrt{\frac{D}{K}} \left[\left(Kt + \frac{1}{2} \right) \text{erf} \sqrt{Kt} + \sqrt{\frac{Kt}{\pi}} e^{-Kt} \right] \quad (41)$$

$$Q = C^* \sqrt{\frac{D}{K}} \left(Kt + \frac{1}{2} \right). \quad (42)$$

One would expect from Table 3 that the $Q_{v,t}$ plot to be linear with a slope of $C^* \sqrt{KD}$ until the depletion of the OH⁻ near the surface which disturbs the first order character of the reaction and makes it impossible to deduce the velocity reaction constant from the observation.

Table 1 shows that at higher exposure time, the absorption rate is governed by the diffusion of OH and CO₂ to the reaction site with effective diffusivity of HO been twice that of CO₂ which is as expected to be less than the self-diffusivity of OH in the same solution. It is also observed that the formation of HCO₃⁻ near the surface also complicated the calculation of absorption rates which was found from this work to be less than 7^{1/2}. From the same table it can also be deduced that the rate of absorption of CO₂ in NaOH solution is not proportional to C* and the true absorption rate of CO₂ observed in this case was 3% less than the observed rate of passage of moist CO₂, and the solubility is 3% less than that of dry CO₂, at atmospheric pressure.

Conclusion

Mathematical modeling of a gas absorption packed column carbon dioxide sodium Hydroxide system had been performed, a model equation was developed and tested. The result obtained shows that it can be used to predict the quantity of CO₂ absorbed in a given time. And $Q_{v,t}$ plot cannot be linear as expected due to the depletion of OH near the surface which disturbed the first order characteristics of the reaction and makes it impossible to deduce the reaction velocity constant. On the other

hand, the rate of absorption of CO₂ in NaOH was found not to be proportional to C due to diluting effect of CO₂ present in CO₂. Hence, these need to correct it. The true absorption rate of CO₂ is 3% less than the observed rate due to this effect. Packing, which will promote a high interfaces area between the two phases and a high degree of turbulence in the fluid may be employed further.

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Appendix

Q-Basic Program

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REM MODELING OF GAS ABSORPTION COLUMN
REM CARBON (1V) OXIDE-NaOH SYSTEM
REM MOHAMMED ALHASSAN
INPUT "CONCENTRATION AT EQUILIBRIUM"; C
INPUT "DIFFUSIVITY"; D
INPUT "RATE CONSTANT"; K
INPUT "MOLAR MASS"; Mw
INPUT "DENSITY OF GAS"; lg
INPUT "BOTTOM MOLE FRACTION"; Yb
INPUT; ABSORPTION FRACTION; Ea
INPUT; FINAL PRESSURE; Pi
INPUT; INITIAL PRESSURE; Po
INPUT MASS TRANSFER COEFFICIENT; ky
INPUT; INITIAL TEMPERATURE; Ti
INPUT; FINAL TEMPERATURE; Tf
INPUT; VISCOSITY OF LIQUID; Vis
INPUT; ACCELERATION DUE TO GRAVITY; G
INPUT; DENSITY OF LIQUID; P1
INPUT; ZIGMA; Z
INPUT; MASS FLOW RATE OF LIQUID; L
PRINT; t (sec); M; Qvg; Ac; D; hp
FOR t = 30 TO 10800 STEP 30
Q = (C*(SQR (D*K)*(t+1 / (2*K))))
Qvg = Q *Mw / Pg
M = (Qvg *Yb*Ea) / ((1 - Yb) * 22.4)
DPm = (Pi - Po) / (ln (Pi / Po))
A = M / (ky / DPm)
V = A / Pg
P = 1.29 *Ti / Tf
G = Qvg *1.29
Z1 = LOG (Z*P ^ (.16 *Vis) / (G
*(V^3)*P1))
Z2 = 1.75 * ((L / G) ^ .25)*(P / P1)
^.125)
VA = SQR ((10 ^ (.022 - Z2 - Z1))
Vc = .075 * Va
Ac = G / (3600*P*Vc)
D = (Ac / .785) ^ .5
hp = Vc / Ac
PRINT tab1
(t);tab3 (M);tab4 (Qvg);tab5 (Ac);tab6 (D)
;tab7 (hp)
NEXT t
END

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Computer Program Algorithm

