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Column Design for Recovery of NH_3 and CO_2 from Wastewater in a Urea Plant

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ABSTRACT

The stripping of CO_2 and NH_3 from chemically reactive dilute aqueous solution in a packed column is modeled using a section-to-section calculation procedure. Equilibrium chemical reaction is accounted for by correcting the liquid film mass transfer coefficient through enhancement factors for the transferring species. Comparison with pilot scale stripping experiments shows that the packed height required for a given separation can be predicted to within 7% on average.

INTRODUCTION

Gas absorption both with and without chemical reaction has been the subject of intensive study for many decades and, although little work has appeared dealing with application to the design and analysis of commercial equipment, especially packed towers, it can now be claimed that the theory at least is well understood (1,2). The reverse step of removing absorbed gases from solutions with which they react is in sharp contrast by remaining virtually unexplored either theoretically or experimentally.

This is a particularity amazing situation in view of the fact that the natural sequel to absorption in any gas purification or recovery process is stripping, a highly energy intensive operation requiring large quantities of steam.

The most prevalent case of desorption in which the transferring species are stripped purely by the action of heat has been addressed recently by Astarita and coworkers (3,4,5) using the film model. The key result of their studies is the delineation of the conditions under which chemical absorption theory can be applied to desorption. More recently, this analysis has been applied to the design from first principles, of continuous contacting equipment for CO_2 removal from spent alkanolamine solutions (6) and model predictions were successfully tested against extensive data taken on a semi-commercial scale column (7). All of this work, however, deals with the transfer of a single reactive species. In the current work we attempt to deal with the simultaneous desorption of carbon dioxide and ammonia from aqueous solution where they are present largely in the form of ammonium carbamate which decomposes under heating. This study was motivated by the need to recover ammonia and carbon dioxide from a waste water stream containing up to three percent of each of these components, emanating from a urea plant.

PROCESS MODEL

Our analysis of the stripping process will be based on the film model of Whitman (8). Although it is generally agreed that this model is not very realistic, it is a matter of experience that predictions based on it are usually very similar to those based on the physically more satisfying penetration theories, and indeed, are identical when all diffusivities are equal. It is common practice in chemical absorption theory to account for the effect of liquid phase chemical reaction through an enhancement factor ϕ. This is the ratio of absorption rates with and without chemical reaction when resistance to mass transfer resides solely within the liquid phase. Then the molar flux of the i-th component is

$$R_i = \phi_i \, k^o_{x,i} \, (x_i - x^*_i) \; ; \; i=1,2 \qquad (1)$$

in which the asterisk refers to the mole fraction at the interface; in the absence of gas phase resistance, this would be determined directly through an equilibrium relation such as Henry's law. If the gas side offers significant resistance, then the molar flux is also given by

$$R_i = k_{y,i} \, (y^*_i - y_i) \; ; \; i=1,2 \qquad (2)$$

Thus, provided $k^o_{x,i}$, $k_{y,i}$, ϕ_i, bulk phase concentrations and equilibrium relations (i.e., solubilities) are known, Eqs. (1) and (2) can be solved iteratively for the interfacial concentrations x^*_i and y^*_i, hence the molar fluxes R_i. The net result would be a *point* value for the desorption flux which could be used in a sequential calculation from point to point along the height of a packed column. It should be noted that the mole fractions x_i refer to the physically dissolved but *unreacted* transferring species, and that an interative procedure would be required because the enhancement factors ϕ_i themselves depend on interfacial concentrations in a nonlinear way. The implication is that the thermodynamics of the equilibrium chemical reaction must be known and this will considerably complicate the calculations.

As outlined by Astarita and Savage (3), the validity of such a model is subject to the following conditions being met: (i) mass transfer lies within or between the diffusional and fast reaction regimes, (ii) there is only a single overall reaction, (iii) the total capacity of the liquid for dissolved gas greatly exceeds its purely physical (e.g., Henry's law) capacity, and (iv) the gas phase composition is linearly related to the concentration of dissolved but *unreacted* gas. These conditions are certainly met in the CO_2-NH_3-H_2O system, especially at the elevated temperatures used in stripping.

Mass and Energy Balances

We consider dividing the column into a number of short sections of height Δz; a typical one is shown in Fig. 1. Calculations might start from the top of the column where the liquid rate and composition entering and the vapor rate and composition leaving are known from process specifications or estimated from overall mass balances. It is evident that on entering the j-th section all conditions at the *top* of that section are known. Ideally, transfer rates should be based on *average* flows and compositions within the section and we are led to the following equations:

$$\bar{N}_{i,j} = \bar{\phi}_{i,j}\, \bar{k}^{o}_{xi,j}\, a(\bar{x}_{i,j} - \bar{x}^{*}_{i,j})\, \Delta z \;;\; i=1,2 \qquad (3)$$

$$\bar{N}_{i,j} = \bar{k}_{yi,j}\, a(\bar{y}^{*}_{i,j} - \bar{y}_{i,j})\, \Delta z \;;\; i=1,2 \qquad (4)$$

with the solubility relations

$$y^{*}_{i,j} = H_{i,j}\, x^{*}_{i,j} \;;\; i=1,2 \qquad (4)$$

In general, Henry's law constant $H_{i,j}$ would depend not only on the particular species involved but also on the concentrations of

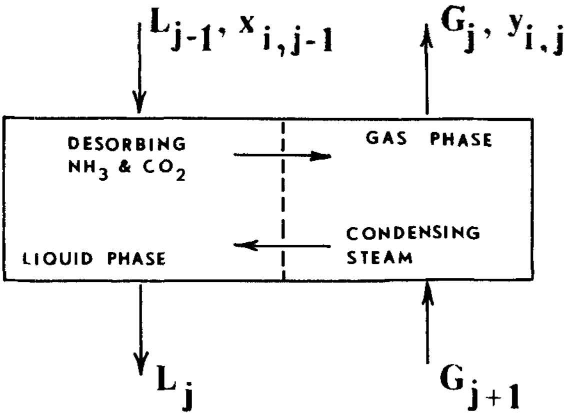

FIGURE 1. Flows and compositions around the j-th section of height Δz.

other species through salting-in and salting-out effects.

Because the liquid is everywhere at its boiling point, any section always operates isothermally; yet, the decomposition of ammonium carbamate is highly endothermic. It is evident that this heat requirement can be met only by condensing part of the vapor phase, specifically, part of its steam content. Thus, in addition to carbon dioxide and ammonia transferring to the vapor phase, steam condenses at the interface and dilutes the liquid. The diffusive fluxes into and out of the liquid phase are nearly equimolar so that diffusive interaction effects can safely be ignored. In any case, basic data such as transfer coefficients are not very accurately known and inclusion of interactive effects would be an unnecessary embellishment.

Physicochemical parameters such as enhancement factors, mass transfer film coefficients and interfacial area are flow and composition dependent so the calculations within a section must be iterative. Having estimated the desorption rates $\overline{N}_i$, we are now in a position to calculate the steam condensation rate $\overline{S}_j$ from an enthalpy balance

$$\lambda_s \overline{S}_j = \Delta H_R[(x_p\ L)_{j-1} - (x_p\ L)j] + \sum_i \Delta H_{s,i} \overline{N}_{i,j} \tag{6}$$

Overall mass balances on the liquid and vapor phases lead to the following equations for liquid and vapor flows at the bottom of the section:

$$L_j = L_{j-1} + \overline{S}_j - \sum_i \overline{N}_{i,j} \tag{7}$$

$$G_{j+1} = G_j + \overline{S}_j - \sum_i \overline{N}_{i,j} \tag{8}$$

and species balances lead to

$$x_{i,j} = [(x_i\ L)_{j-1} - \overline{N}_{i,j}] \ /\ L_j \ ;\ i=1,2 \tag{9}$$

$$y_{i,j+1} = [(y_i\ G)_j - \overline{N}_{i,j}] \ /\ G_{j+1} \ ;\ i=1,2 \tag{10}$$

A first estimate of the desorption rates $\overline{N}_{i,j}$ can be obtained by assuming all flows and compositions to be constant within the section and equal to their values at the top. The solution to Eqs. (3) to (5) is then used in Eqs. (6) to (10) to obtain first estimates of bottom conditions. Note that once the $\overline{N}_{i,j}$ have been found, the remaining equations can be solved sequentially. Further iterates are based on the averages

$$\overline{L}_j = \tfrac{1}{2}(L_{j-1} + L_j) \qquad (11)$$

$$\overline{G}_j = \tfrac{1}{2}(G_j + G_{j+1})$$

and similar quantities for the mole fractions. If coarse sectioning is used then it is probably better to use logarithmic mean mole fractions but for relatively short sections, arithmetic means are adequate. Calculations proceed from section to section until conditions at the bottom of the column are reached. Finally, one might repeat the entire procedure over the whole column using a larger number of shorter sections to ensure that accuracy has not been sacrificed by partitioning that is too coarse.

It should be noted that diffusive interaction between transferring species has been ignored; the only coupling is provided through the liquid phase chemical reaction and we have avoided a description of the process in terms of a film model solution of the Maxwell-Stefan equations for example. In view of the large uncertainty in most of the physicochemical data necessary to these calculations, an interactive multicomponent description would be needlessly sophisticated.

Kinetics, Enhancement Factors and Equilibrium

Although there are a number of chemical species present in solution, including carbonate and bicarbonate ion, the predominant species may be considered to be in the form of dissolved CO_2 and NH_3 and the reaction product ammonium carbamate. The overall reaction is (9)

$$2NH_3\ (aq) + CO_2\ (aq) \rightleftharpoons NH_3COONH_3 \qquad (12)$$

The rate controlling step, however, is (10)

$$NH_3\ (aq) + CO_2\ (aq) \rightleftharpoons NH_2COOH \qquad (13)$$

so that the chemical kinetics are second order. Nevertheless, equilibrium is governed by reaction (13).

Enhancement factors for carbon dioxide and ammonia have been derived by Rod and Rylek (10) based on the film model and the assumption that chemical equilibrium prevails everywhere in the liquid phase, including the liquid film. The enhancement factor for CO_2 was found to be

$$\phi_{CO_2} = \frac{Ha}{\tanh(Ha)} \qquad (14)$$

where Ha is the Hatta number

$$Ha = (k_R\ C^*_{NH_3}\ D_{CO_2} / k^{o2}_{L,CO_2})^{\frac{1}{2}} \qquad (15)$$

and the corresponding expression for ammonia is

$$\phi_{NH_3} = 1 + \frac{D_{CO_2}}{D_{NH_3}} \cdot \frac{C^*_{CO_2} - C_{CO_2}}{C^*_{NH_3} - C_{NH_3}} (\phi_{CO_2} - 1) \qquad (16)$$

where the asterisk again refers to the gas-liquid interface and these concentrations must be calculated from chemical reaction equilibrium and physical solubility data.

Equilibrium data for the CO_2-NH_3-H_2O system at the elevated temperatures common in stripping are available (11) in the form of a series of plots of the equilibrium partial pressures of carbon dioxide and ammonia against the fractional saturation of the liquid phase (carbonation ratio, equal to total moles CO_2 per mole NH_3, both species in all forms) with total ammonia concentration and temperature as parameters. In the mass transfer calculations, the bulk liquid-phase carbonation ratio and ammonia concentration are known; hence, chemical equilibrium data are used to determine the gas-phase partial pressures which would be in equilibrium with the bulk liquid. Then Henry's law for the species involved provides a route back to the liquid phase and gives the concentrations of the physically dissolved but unreacted species. The same calculations must be done of course for the interfacial concentrations, but now these are tied to the mass transfer rates through Eqs. (3) and (4) which makes the whole procedure iterative.

Equilibrium data in the above form are not very suitable for direct use in these computations - there are three independent variables and certainly one would expect temperature dependence to be expressible in the form A exp ($\Delta H/RT$). Unfortunately, data are usually obtained by varying the carbonation ratio while holding temperature fixed rather than vice-versa. Therefore, the procedure adopted was to pass the best least-squares polynomials through the data as reported, and then build up cross-plots of solute partial pressure versus 1/T with carbonation ratio as parameter, which could be correlated as straight lines. This reduced equilibrium calculations to two-parameter interpolation.

Physicochemical Data

Correlations for individual film coefficients for mass transfer have been presented elsewhere (12) for various packing sizes and types. For ½-in. Raschig rings (the packing used in the experiments)

$$k_x a = 145\ (L/\mu_L)^{0.89}\ (\mu_L/\rho_L\ D_L)^{0.5}\ D_L \tag{17}$$

while the gas-side coefficient for ammonia is correlated by (12)

$$k_y a = 0.145\ G^{0.9}\ L^{0.39}\ P \tag{18}$$

The Schmidt number is the parameter commonly used to estimate gas-film coefficients for other gases from data on ammonia.

The heat of the overall reaction for carbamate formation from reactants in the dissolved state is reported (13) to be -13.1 kcal/gmol at infinite dilution. Since our interest is in recovery from dilute solution, no correction for concentration effects was made. The heat of desorption of ammonia from water is 0.617 times the latent heat of vaporization of water (14) and Danckwerts (2) reports 4.76 kcal/gmol as the heat of solution of CO_2 into water.

The rate constant k_R for the forward reaction in Eq. (14) appears in Eqs. (15) and (16) for the enhancement factor for CO_2. The following temperature dependence has been found by Andrews (15):

$$\log_{10} k_R = 14.23 - 2550/T \tag{19}$$

with k_R in the units (cm^3/gmol s) and T in K.

Finally, other fundamental data including diffusion coefficients, solvent viscosity, dew points and Henry's law constants have been taken from Rawal (16) and Perry (17) as correlations for temperature dependence.

EXPERIMENTAL

A layout of the pilot plant used for experimental measurements of stripping rates is shown in simplified schematic form in Fig. 2. Only major equipment items and process streams are indicated; valving arrangements, instruments for the measurement of flow rate, temperature and pressure, cooling water lines and steam lines have been omitted. However, a detailed description may be found elsewhere (16).

A metered flow of carbonated ammonia solution was passed via a gear pump to a steam heated U-tube exchanger H of 0.5 m^2 area where it was preheated to the boiling point at the prevailing stripper pressure. The boiling, rich liquor entered the top of the stripping column S and was distributed over the packing through a five-legged spider arrangement. The stripper was 15.2 cm (6-in.) in diameter packed to a height of 1.64 m with 12.7 mm (½ -in.) Raschig rings of wall thickness approximately 3 mm. Thus, the column to packing diameter ratio was 12. Vapor was provided by a 1 m^2 vertical thermosyphon reboiler operating at high recirculation and its flow was controlled by the steam pressure on the shell side of the reboiler. Bottoms from the column joined the recirculation loop and part of the total flow was drawn off at

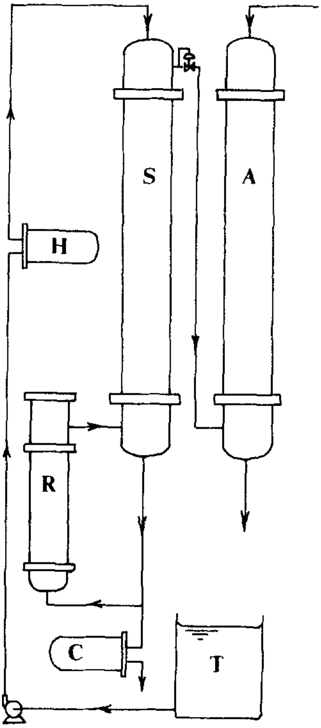

FIGURE 2. Schematic of pilot plant.

a measured rate so as to maintain constant liquid level at the base of the column. This lean liquor was cooled in the 0.5 m^2 U-tube exchanger C before being sewered.

Vapor, composed of steam, carbon dioxide and ammonia was released from the column through an air-to-close pneumatically actuated valve which controlled the stripper pressure; it passed at substantially atmospheric pressure via an orifice meter to the base of the condenser-reabsorber A. There the vapor met a countercurrent flow of cold water which condensed the steam and completely reabsorbed the carbon dioxide and ammonia. This stream was also sewered. No particular care was taken in packing the reabsorber and it contained a variety of packing types and sizes; its sole purpose was to prevent release of the stripped gases to atmosphere.

Process Measurements

Temperatures at various points in the process were monitored with iron-constantin thermocouples in stainless steel sheaths referenced to an ice bath. The feed temperature leaving the preheater H was measured and controlled by manually adjusting the shell-side steam pressure and thermocouples were inserted 15 cm above and below the bottom and top, respectively, of both packed columns.

Liquid flow rates to and from the stripper were measured with metric-series rotameters and the vapor flow leaving the column was monitored with an orifice meter situated between the pressure letdown valve and the reabsorber.

Samples of the feed stream to the stipper and of the liquid stream leaving the packing support plate were analyzed for CO_2 and NH_3 by potentiometric titration after addition of barium chloride to the sample to first precipitate the carbon dioxide. Two inflection points in the pH curve were found at pH 7-8 (ammonia) and pH 3-5 (carbon dioxide). Vapor samples were not taken so no check was made for closure of a mass balance; however, previous work (17) with the CO_2-monoethanolamine system suggests that closure to within ±22% can be expected on average. Since *measured* flow rates and compositions are to be used as input data to the process model, we anticipate that the *predicted* column height required to perform the measured task will be in no better agreement with the actual height than the extent to which a mass balance closes.

RESULTS AND DISCUSSION

Rather than providing an extensive set of measured column performance data which, in any case, would be limited to Raschig rings of commercially unimportant size (½-in.), the purpose of the experiments was to provide confirmation (or otherwise) of the model. Results of the rather limited number of experiments conducted are given in Table 1 from which it can be seen that

TABLE 1

Summary of Experimental Results

Experiment	Pressure (Atm)	Feed Rate (kg/m)	Top Vapor Rate (kg/m)	Feed Composition		Bottoms Composition	
				w/w% NH_3	w/w% CO_2	ppm NH_3	ppm CO_2
1	2.13	3.78	0.40	1.89	0.79	930	27
2	2.13	2.34	0.29	1.44	0.24	100	20
3	2.13	3.11	0.29	1.46	0.38	640	130
4	2.13	2.29	0.29	1.42	0.91	110	20
5	3.25	2.34	0.29	1.49	0.39	200	30
6	2.90	2.34	0.36	1.37	0.83	55	6

ammonia and carbon dioxide concentrations as low as 55 ppm and 6 ppm, respectively, were achieved. An overhead vapor containing up to 20 w/w % ammonia was produced. It is also interesting to note that CO_2 can be stripped much more easily than ammonia. System parameters such as pressure were not varied in such a way as to show the effect of one variable at a time; hence, it is not possible from these rather sparse data to comment on the response of the system to a change in only one operating condition. However, these data do provide a reasonable basis for comparison with model predictions.

The fundamental model outlined earlier was programmed in Fortran for the prediction of column height required to produce a specified lean bottoms composition from a given feed concentration and rate when the column operating pressure and overhead vapor rate (directly related to the boilup rate) are stipulated. Mass and energy balances are determined for each section and the calculations proceed sequentially from section to section. Within any section mass transfer rates are established by iterative calculation. A comparison between the predicted and experimental column height required to perform the separations indicated in Table 1 is presented in Table 2. The experimental packed height

TABLE 2

Predicted Column Height

Experiment	Height (m)
1	1.5_1
2	1.4_8
3	1.8_5
4	1.7_3
5	1.2_5
6	1.3_0

Mean = 1.5_2m, $\sigma = \pm 0.2_3$m

was 1.64 m; the predicted height for these six experiments was 1.52 m with a standard deviation of ±0.23 m or 15%.

A similar model has been analyzed by Hegner and Molzahn (18) who set up the problem in terms of a block tridiagonal matrix formulation rather than the sequential section-to-section procedure described here. These formulations are entirely different since the matrix approach requires that the height of the column be a known quantity; whereas, sequential methods calculate it as part of the solution procedure. Nevertheless, matrix methods form a cornerstone in the analysis of staged operations.

In the present case, for which flows and compositions can be completely specified for the feed and closely estimated for the overhead vapor, section-to-section methods are recommended over block tridiagonal matrix formulations (19). Matrix methods were originally developed to overcome convergence difficulties experienced with the sequential procedures in certain types of problems involving equilibrium stage calculations. The extension to continuous contacting equipment by Hegner and Molzahn (18) is a commendable contribution, that needs to be explored in much greater depth, not only for continuous contacting equipment, but also for *non*equilibrium stage operations in which each component may have a different composition-dependent stage efficiency.

These authors compared their calculations with experimentally determined vapor-phase CO_2 and NH_3 mole fractions and found that CO_2 predominated at the base of the column, being at very low concentrations near the top where ammonia was the dominant component. Our findings are contradictory in that we observed both CO_2 and ammonia to be in exceedingly low concentration at the bottom of the column. However, our experiments were carried out at pressures up to 33 psig and temperatures up to nearly 140°C whereas those of Hegner and Molzahn were done at 0 psig and a correspondingly lower temperature. Thus, rather unfavorable rates of carbamate decomposition could be expected in their work.

In summary, a section-to-section procedure has been proposed for the design and analysis of packed columns for the recovery of ammonia and carbon dioxide from a waste water stream. Model predictions have been validated by comparison with several pilot scale experiments. It is also of interest to note that by having a fundamental or mechanistic model available, one is in a position to optimize column design, to enable operation at minimum energy consumption rates, for example.

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NOTATION

a	interfacial area (m^2/m^3)
C	concentration ($kgmol/m^3$)
D	diffusion coefficient (m^2/s)
G	vapor rate (kg/m^2 s)
H	Henry's law constant
Ha	Hatta number
ΔH_R	heat of reaction (kcal/gmole) or (J/kgmol)
ΔH_S	heat of solution (J/kgmole)
k_R	reaction rate constant ($cm^3/gmol \cdot s$)

$k_x^o a$	liquid-film coefficient without reaction ($kgmol/m^3$ s)
$k_y a$	gas-film coefficient ($kgmol/m^3 \cdot s$)
L	liquid rate ($kg/m^2 \cdot s$)
N	molar mass transfer rate (kgmol/s)
P	system pressure (atmospheres)
R	molar flux ($kgmol/m^2$ s)
S	steam condensation rate (kgmol/s)
T	absolute temperature (K)
x	mole fraction in liquid phase
y	mole fraction in gas phase
Δz	height of a section (m)

Greek Letters

λ_s	latent heat of condensation of steam (J/kgmol)
μ	viscosity (kg/m•s)
ρ	density (kg/m^3)
ϕ	enhancement factor

Superscripts

*	equilibrium
—	average

Subscripts

i	component
j	section
p	carbamate

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