

## SELECTIVE REMOVAL OF CARBON DIOXIDE FROM AQUEOUS AMMONIA SOLUTIONS

Jan F. Maćkowiak<sup>1</sup> and Andrzej Górak<sup>2</sup>

<sup>1</sup> ENVIMAC Engineering GmbH, Im Erlengrund 27, 46149 Oberhausen, Germany,  
Email: jan.mackowiak@envimac.de

<sup>2</sup> TU Dortmund, Chair of Fluid Separations, 44221 Dortmund, Germany

### Abstract

In this work modelling and experimental validation of an integrated process for the removal of carbon dioxide from ammonia solutions is presented (decarbonisation). In this process, carbon dioxide is stripped out from the solution simultaneously with small amounts of ammonia at ambient pressure in a packed column. Recovery of the stripped ammonia can be reached by combining absorption of ammonia and condensation of stripping steam. The interaction of the different unit operations of stripping, absorption and direct-contact condensation (DCC) can be arranged in one single packed column where stripping takes place in the lower part of the column, and the DCC and ammonia absorption in the upper part. To describe the process a rigorous model based on the film theory which considers heat and mass transfer as well as reaction rates directly has been adapted to the requirements of multicomponent reactive stripping, absorption and direct-contact condensation in packed columns<sup>1</sup>. Extensive experimental investigations have been performed for both, the stripping and for the direct-contact condensation in a pilot scale packed column with diameters of 0.15 and 0.32 m. Relevant operation parameters as well as column dimensions were varied during the experiments in order to achieve a broad data base for the validation. Experimental validation of the two sub-processes and the entire decarbonisation shows good agreement between calculated and experimental values. Based on the validated model a successful optimisation of the decarbonisation process has been performed, leading to increased carbon dioxide removal and reduction of ammonia losses.

**Keywords:** condensation, absorption, stripping, rate-based modelling, carbon dioxide, ammonia

### 1. Introduction

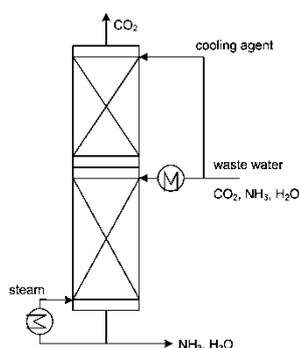
Waste water containing ammonia (NH<sub>3</sub>) and carbon dioxide (CO<sub>2</sub>) is part of numerous processes in chemical, petrochemical, food and environmental industry. Recently it becomes more significant in biogas production from renewable resources. In many cases ammonia can be recovered from the waste water and converted into valuable products. Usually, air or steam stripping is applied for the ammonia removal complemented by biological denitrification. Desorption via stripping requires a pH value higher than 10 in order to shift the ammonia dissociation equilibrium (eq. 1) to molecular species.



Alkaline solution, mostly caustic soda, is often added to the waste water in order to keep the pH on the right level, although it is undesirable from the economic and environmental point of view. The presence of carbon dioxide leads to an even increased demand of the caustic soda demand because of the acidic nature of carbon dioxide. This often leads to economically infeasible ammonia recovery processes. If carbon dioxide is selectively removed from the waste water, the pH-value is raised due to the deacidification effect without adding chemicals. Selective carbon dioxide removal (decarbonisation) prior to the actual ammonia stripping is therefore beneficial.

In the decarbonisation stage, carbon dioxide is stripped out from the solution simultaneously with ammonia at ambient pressure. Recovery of the stripped ammonia can be reached by combining absorption of ammonia and condensation of stripping steam (see Figure 1). The interaction of the different unit operations of stripping, absorption and direct-contact condensation (DCC) can be

achieved in one single packed column (DecaStripp<sup>®</sup>-process). The decarbonisation column consists of two sections which are directly interconnected. In the lower section, the preheated solution is fed in on top and steam flows counter-currently from the bottom, carrying the desorbed components toward the upper part. In the upper section, the steam is condensed directly into the condensing agent and ammonia is absorbed by the liquid, while the low soluble carbon dioxide remains in the vapour phase and leaves the column at the top. A high selectivity of the CO<sub>2</sub> removal is desired in the desorption part in order to reduce complexity of the condensation process. The decarbonised solution leaves the column at the bottom and can be further treated in order to recover ammonia. The efficiency of the entire ammonia recovery process is significantly affected by the design of the decarbonisation stage.



**Figure 1.** Decarbonisation process for selective carbon dioxide removal at ambient pressure

The modelling of this complex integrated process requires an adequate, experimentally validated modelling framework. The application of the rate-based approach for the modelling of multicomponent reactive separation processes has proved to be superior to other concepts like the equilibrium stage model. The rate-based approach is physically more consistent and overcomes the drawbacks of multicomponent efficiencies and HETP values. The relevance of a model which shall be used for design purposes is highly affected by the quality of available experimental data used for the model validation. For many relevant industrial processes, data from the literature is scarce. The same is true for the NH<sub>3</sub>-CO<sub>2</sub>-H<sub>2</sub>O system, especially in connection with a selective carbon dioxide removal from aqueous solutions. In order to provide data for the presented model extensive experiments have to be performed.

## 2. Rate-based Modelling

The key element of the rate-based model is an axial segment of a packed column in which simultaneous mass transfer and chemical reactions are described according to the extended film model (see Figure 2). The model is based on separately formulated mass and heat balances for the vapour and liquid phases. These balances are linked by the interfacial heat and mass fluxes,  $E$  and  $N_i$ , which are equal for both phases. Thermodynamic equilibrium between the phases is assumed at the interface. According to the film model, the resistance to mass and heat transfer is placed in thin films adjacent to the phase boundary. Chemical reactions in the system NH<sub>3</sub>-CO<sub>2</sub>-H<sub>2</sub>O influence the ammonia and carbon dioxide concentrations in the liquid phase and thus the gas-liquid equilibrium. Reaction equilibrium and kinetics are considered in both the liquid film and bulk phase.

In multicomponent mixtures the component fluxes across the interface are usually calculated using the Maxwell-Stefan equations, which consider these effects. In this work, the linearized theory presented by Toor<sup>2</sup> and Stewart and Prober<sup>3</sup> has been applied to handle the Maxwell-Stefan equations for the diffusive mass transfer in the film region. Its main assumption, which has proven to be of excellent accuracy for the majority of mass transfer processes, is that diffusion coefficients remain constant in the film region. Several works<sup>4-6</sup> show that simplified models like the effective diffusivity method are sufficient in order to describe most reactive absorption and desorption processes because of negligible diffusional interactions between components. The complexity of the model and calculation time can therefore be reduced. This assumption holds as well for the desorption process often applied in decarbonisation of waste water. A detailed comparison of the two models showed, that deviations between the two calculation methods can be neglected<sup>1</sup>.

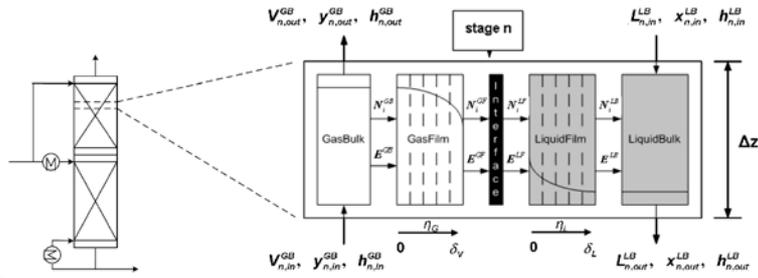


Figure 2. Structure of an axial segment of the column according to the film theory

This does not hold for multicomponent DCC, which is used in the decarbonisation process. Here, the ternary vapour phase is usually not diluted and diffusional interactions may not be neglected. Deviations in mass transfer fluxes between the Maxwell-Stefan and the effective diffusivity method increase for the DCC compared to the desorption process. This causes, for practical purposes even more important, a significant difference between the calculated vapour outlet concentrations of ammonia, carbon dioxide and water which in some cases exceeds 25 %. These deviations which have been observed during the theoretical analysis of the process<sup>1</sup>, can be regarded as critical for column design, especially when ammonia emission limits have to be obeyed. Therefore the effective diffusivity method is applied to calculate mass transfer fluxes in the stripping section and the Maxwell-Stefan equations for the DCC section in the decarbonisation process.

The models have been implemented into the commercial simulation environment Aspen Custom Modeler<sup>®</sup>, which provides a fully numerical algorithm to solve the system of rate-based equations. The simulation tool offers a direct link to the software package Aspen Properties<sup>®</sup> for the calculation of the required physical properties. A subdivision of the liquid and the gas/vapour film into discrete elements allows the description of the nonlinear concentration and temperature profiles. Packing specific fluid dynamics<sup>7</sup>, relevant mass transfer correlations<sup>8</sup> and the component specific reaction rates are accounted for by adequate sub-models. The description of external elements like reboilers and heat exchangers complement the model. Detailed model equations are shown elsewhere<sup>1</sup>.

### 3. Experimental Analysis

In order to provide relevant data for a model validation, an extensive experimental investigation has been performed in pilot scale packed columns. Therefore desorption by steam stripping and the DCC process were studied separately.

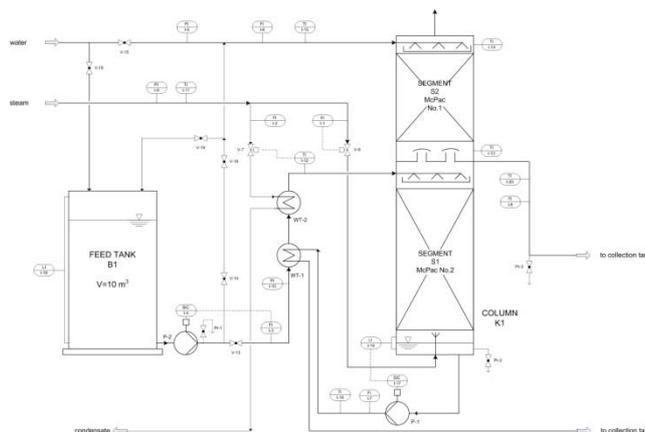


Figure 3. Experimental set up for the investigation of desorption (steam stripping) and direct-contact condensation processes in the  $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$  system

Both processes have been integrated in one steel column with a column diameter of  $d_{c,S} = 0.316$  m and  $d_{c,C} = 0.150$  m and a total height of up to 10 m, see Figure 3. The pilot plant is equipped with state-of-the-art measurement devices and a highly automated Siemens S7 process control system. This

allows a high accuracy of the experiments, shown by the adequate relative deviation in total mass balance of maximal  $\pm 4\%$  and  $\pm 8\%$  for both the ammonia and carbon dioxide liquid side balance. The ammonia concentrations in the liquid phase have been detected by a photometer, the carbon dioxide contents by titration. McPac<sup>9</sup> high performance packings of two different sizes have been chosen as random packings for the tests. The size of the test columns requires an appropriate amount of feed solution, which therefore was produced by dissolving  $\text{NH}_4\text{HCO}_3$  in the  $10\text{ m}^3$  feed tank. The feed concentration of ammonia  $c_{\text{NH}_3}$  varied between 2 and 5 g/l, which is typical for many kinds of waste waters, e.g. from biogas or coking industry. The main objective of the desorption part is a high selectivity of carbon dioxide compared to ammonia removal efficiency. The selectivity  $S_{\text{CO}_2, \text{NH}_3}$  is calculated based on the removal efficiencies  $\mathfrak{g}_i^D$  as follows:

$$S_{\text{CO}_2, \text{NH}_3} = \frac{\mathfrak{g}_{\text{CO}_2}^D - \mathfrak{g}_{\text{NH}_3}^D}{\mathfrak{g}_{\text{CO}_2}^D + \mathfrak{g}_{\text{NH}_3}^D} \quad \text{with} \quad \mathfrak{g}_i^D = 1 - \frac{\dot{N}_{i, \text{in}}^L}{\dot{N}_{i, \text{out}}^L} \cdot 100\% \quad (2)$$

The superscript *D* denotes that efficiency refers to the desorption process. In order to analyse the separation efficiency of the stripping part, the influencing parameters like liquid and vapour load, packing height and type, feed concentration and temperature were varied over a wide range (Table 1). The vapour mixture of the desorption section is used as feed for the DCC section. This leads to a database consisting of 50 data records for the desorption process and 39 for the DCC process.

**Table 1.** Varied parameters during the experimental analysis of the desorption and DCC process using lattice type McPac 1 and 2 random packings

Desorption & DCC	symbol / unit	range
segment diameter	$d_{c,i}$ [m]	0.15 - 0.316
Liquid load	$u_L$ [ $\text{m}^3\text{m}^{-2}\text{h}^{-1}$ ]	6 - 26
Gas capacity factor	$F_V$ [ $\text{Pa}^{0.5}$ ]	0.1 – 2.5
liquid feed concentrations (desorption)	$c_{\text{NH}_3}^{\text{in}} / c_{\text{CO}_2}^{\text{in}}$ [mol/l]	(0.12-0.31) / (0.08-0.27)
vapour feed concentrations (DCC)	$y_{\text{NH}_3}^{\text{in}} / y_{\text{CO}_2}^{\text{in}}$ [vol.-%]	(1-20) / (2-26)
McPac random packings	$a$ [ $\text{m}^2\text{m}^{-3}$ ] / $\varepsilon$ [ $\text{m}^3\text{m}^{-3}$ ]	90-185 / 0.97
Liquid feed temperature	$T$ [ $^\circ\text{C}$ ]	80 - 98

The gas and liquid load has significant influence on the selectivity of ammonia and carbon dioxide removal from the liquid. Mass transfer of  $\text{NH}_3$  in the binary  $\text{NH}_3\text{-H}_2\text{O}$  system is known to be controlled by gas and liquid side resistance, thus vapour load has a larger influence on ammonia removal compared to the system  $\text{CO}_2\text{-H}_2\text{O}$ , which is basically controlled by the liquid side resistance. Although, the observed dependency on the inlet concentration ratio of the two components cannot be explained by consideration of only binary mass transfer effects. As a consequence, the carbamate-reaction between ammonia and carbon dioxide (eq. 3) should not be neglected even at high temperatures of up to  $100^\circ\text{C}$ .

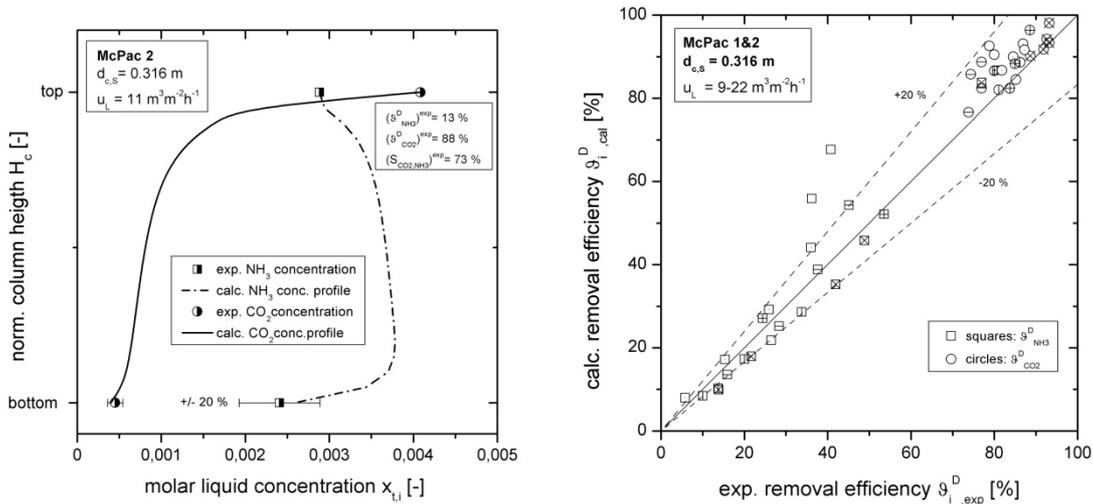


The sensitivity of packing size and height on mass transfer is not as distinctive as the operation parameters mentioned above. It can be summarised that selectivity for the carbon dioxide removal via steam stripping can be increased up to 90 % under the tested conditions. Compared to the DCC of pure vapours, which has been experimentally investigated in a different work<sup>10</sup>, the presence of  $\text{NH}_3$  and  $\text{CO}_2$  affects noticeably the condensation of steam in the multicomponent mixture. As the  $\text{CO}_2$  solubility in water, which is used as condensing agent, is low, it can be regarded as a quasi-inert, which increases the mass transfer resistance in the vapour phase compared to the pure vapour. Therefore,

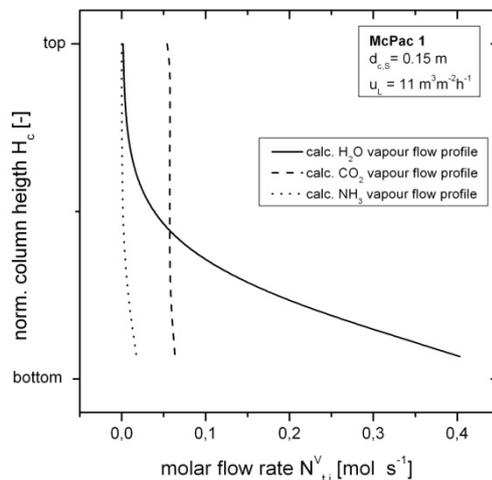
the condensation efficiency decreases with increasing inert concentration what has to be considered during the design of the packed bed condenser.

#### 4. Model validation

Based on the experimental results data reconciliation has been performed in order to provide consistent input data for the simulations. Therefore the measured flow rates and concentrations were varied within their specific tolerances until consistent component balances were achieved. The presented rate-based allows for the description of concentration profiles along the packed column. A comparison of calculated concentration profiles and experimental output and reconciled input values for a desorption experiment is shown in Figure 4a. It shows that most of the carbon dioxide is already desorbed near the top of the column. Even low carbonate concentrations cause an increased chemical demand in the following ammonia removal steps, thus the bed length should be long enough to achieve maximum removal efficiency. Figure 4b shows a parity plot for all desorption experiments based on removal efficiencies of both ammonia and carbon dioxide. It can be stated that the model reproduces the experiments within a maximum deviation of  $\pm 20\%$  for the conditions shown in Tables 1 and 2. The model can therefore be used for design as well as for optimisation of the desorption process.



**Figure 4.** a) Concentration profile of NH<sub>3</sub> and CO<sub>2</sub> along the packed bed for a typical desorption experiment. b) Parity plot for all performed desorption experiments compared to the rate-based model based on removal efficiencies according to eq. (2).



**Figure 5.** Flow profile of NH<sub>3</sub> and CO<sub>2</sub> along the packed bed in the DCC section

This holds as well for the DCC in packed columns, where so far no reliable data for multicomponent condensation has been published. The experiments can be reproduced with a similar precision as the Desorption experiments. Figure 5 shows a typical flow profile of the components during DCC in the scope of decarbonisation of waste water from biogas and coking industries. Molar flows are chosen to display the condensation and selective absorption along the packed bed because total flow of the vapour decreases significantly during the condensation process.

## 5. Conclusions

A process for the selective removal of dissolved carbon dioxide from ammonia solutions (decarbonisation) has been presented. The process consists of two steps, a desorption part, where carbon dioxide is stripped by means of steam and a DCC part, where the steam is condensed and eventual gaseous ammonia is absorbed in a packed column. To describe the reactive multicomponent separation processes a rate-based model for both steps has been developed based on previous works. The model has been implemented into Aspen Custom Modeler and features Maxwell-Stefan equations to handle multicomponent mass transfer for the DCC process as well as the simplified effective diffusivity method which can be applied with high accuracy for desorption processes in the system  $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$ . An extensive experimental analysis of both desorption and the DCC identified the sensitive operating parameters influencing the selectivity of carbon dioxide to ammonia removal for the desorption and the DCC. The experiments have been performed in pilot scale packed columns with diameter from 0.15 to 0.316 m and a total column height of up to 10 m. Input concentrations of ammonia and carbon dioxide and the vapour and liquid load have great influence on the selectivity of carbon dioxide removal. In contrast to the binary system  $\text{CO}_2\text{-H}_2\text{O}$ , in which transfer resistance is located mainly the liquid phase, the vapour load affects the ammonia removal significantly. The ammonia removal efficiencies thus vary from 3 to 80 % depending on the operation point of the column. As a result, selectivities of up to 90 % can be achieved in the decarbonisation process, resulting in an increase of the outlet pH-value of up to 10.5, which is high enough to reduce the chemical demand in the following ammonia removal step by 90 %.

The experimental data has been successfully used to validate the models, which is characterised by a satisfying accuracy under the studied conditions of max.  $\pm 20$  %. The range of operating conditions and the number of 50 data sets for the desorption and 38 sets for the DCC allow a most convincing validation for reactive stripping and direct contact condensation in packed columns resulting in a powerful tool for optimisation and design purposes.

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