

Chapter 4

**MASS TRANSFER IN AMINE-BASED CO₂
ABSORPTION PROCESS: THEORY AND ITS
APPLICATIONS TO PLANT DESIGN AND OPERATION**

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ABSTRACT

This book chapter reviews mass-transfer fundamentals associated with CO₂-amine absorption systems and demonstrates how theoretical knowledge is used for design and operation of large-scale CO₂ absorption columns. The chapter begins with mass-transfer basics presenting mass-flux equations, Two-film theory with an integration of Henry's law, and compilation of Henry's law constant data and/or equations available for various CO₂-amine absorption systems. Three theories, i.e., film, penetration and surface-renewal are described and used to determine mass-transfer coefficient in the liquid film residing next to the gas-liquid interface. The role of chemical reactions between CO₂ and amine on mass transfer is reviewed by compiling series of absorption reactions, kinetic rate constants, reaction regimes and enhancement factor equations. Role of vapor-liquid-equilibrium on mass-transfer driving force in the CO₂ absorption process, including mass-flux analysis and mass-transfer limits due to equilibrium, is discussed. Furthermore, the chapter includes the knowledge of exothermic process operations leading to changes in temperatures and physical properties of both gas and liquid phases within the absorption column and their impacts on mass-transfer efficiency and limits. At the end of this book chapter, a design procedure for gas absorption column in CO₂-amine application and column design simulation results are provided.

Keywords: mass transfer, CO₂ capture, CO₂ absorption, amines, kinetics

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INTRODUCTION

The removal of carbon dioxide (CO₂) from industrial gas streams has been an important step in many process operations such as ammonia production, natural gas purification, and oil refining. In these processes, CO₂ is considered as an impurity that must be removed in order to enhance the quality of gas products. Recently, the CO₂ removal has become one of the crucial strategies that help to reduce the emissions of greenhouse gases generated from fossil-fuel combustion. The removal of CO₂ can be achieved by a number of processes. Among these, gas absorption into amine solutions is the most promising and cost-effective approach for removing CO₂ from high-volume gas streams.

The purpose of this book chapter is to review mass-transfer fundamentals associated with CO₂-amine absorption systems and also to demonstrate how theoretical knowledge is used for design and operation of large-scale CO₂ absorption columns. This book chapter is organized into six sections including i) mass-transfer basics, ii) liquid-side mass-transfer coefficient, iii) role of chemical reactions between CO₂ and amine on mass transfer, iv) role of vapor-liquid-equilibrium (VLE) on mass transfer, v) exothermic energy and mass-transfer operation, and vi) demonstration of the design and operation of CO₂ absorption columns. The section of mass-transfer basics presents mass-flux equations, Two-film theory with integration of the Henry's law, and compilation of Henry's law constant data and/or equations available for various CO₂-amine absorption systems. The section of liquid-side mass-transfer coefficient describes film, penetration and surface-renewal theories used for determination of mass-transfer coefficient in the liquid film residing next to the gas-liquid interface. The section of role of chemical reactions between CO₂ and amine on mass transfer summarizes types of amines available for CO₂ absorption process, and their absorption reactions. A review on kinetic rate constants, reaction regimes and enhancement factor equations together with their application ranges for individual amines is also provided. The section of vapor-liquid-equilibrium discusses the role of vapor-liquid-equilibrium on mass-transfer driving force in the absorption process, mass-flux analysis that combines both equilibrium data and actual operating conditions in CO₂ absorption process and mass-transfer limits due to the equilibrium. The section of exothermic energy and mass transfer operation provides knowledge of the exothermic process operations leading to changes in temperatures and physical properties of both gas and liquid phases within the absorption column and their impacts on mass-transfer efficiency and limits. The last section is dedicated to the design procedure for gas absorption columns in CO₂-amine application, role of packing hydrodynamic features on mass-transfer activities in the full-length absorber. It describes two approaches of the adiabatic column design and presents column design simulation results that generate a comprehensive set of mass-transfer and temperature column profiles along the absorber. A comparison between simulated results and a pilot plant data currently reported in literature was also made.

MASS TRANSFER BASICS

Mass transfer is the phenomenon characterized by the movement of chemical substances from one location to another on a molecular basis. The molecular transport occurs in many

chemical engineering processes, including CO₂ absorption and CO₂ stripping, where the transferring component (CO₂ in this case) travels across the interface between gas and liquid phases. The mass transfer rate and its direction take place by means of diffusion driven by CO₂ concentration gradient being developed over the two insoluble fluids. Mass transfer flux of CO₂ (N_{CO_2}) can be written as:

$$N_{CO_2} = k_G P (y_{CO_2,G} - y_{CO_2,i}) = k_L^o (C_{CO_2,i} - C_{CO_2,L}) \quad (1)$$

where k_G and k_L^o are the gas-side mass transfer coefficient and the liquid-side mass transfer coefficient, respectively; P is the total system pressure; $y_{CO_2,G}$ and $y_{CO_2,i}$ are the CO₂ mole fractions in the gas bulk and the gas-liquid interface, respectively; and $C_{CO_2,L}$ and $C_{CO_2,i}$ are the CO₂ concentrations in the liquid bulk and the interface, respectively. Note that Equation (1) is for mass transfer activity in an absence of chemical reactions. It is commonly assumed that the mass transfer resistances are those residing in the fluids themselves; there is then no resistance to the transfer across the interface [1]. This suggests that the mole fraction $y_{CO_2,i}$ in the gas phase is in equilibrium with the concentration $C_{CO_2,i}$ in the liquid phase. The CO₂ equilibrium can be expressed by Henry's law [2].

$$P y_{CO_2,i} = H_{CO_2} C_{CO_2,i} \quad (2)$$

where H_{CO_2} is the Henry's law constant for CO₂ in the unit of kPa m³ kmol⁻¹.

In the actual absorption operation, it is rather difficult to precisely determine CO₂ concentration at the gas-liquid interface. Thus, it becomes more practical to express the mass transfer flux as a function of bulk concentrations ($y_{CO_2,G}$ and $C_{CO_2,L}$) that can be directly measured from the process operation. This leads to an alternative mass flux equation written in terms of the overall mass transfer coefficients K_G and K_L .

$$N_{CO_2} = K_G (P y_{CO_2,G} - H_{CO_2} C_{CO_2,L}) = K_L \left(\frac{P y_{CO_2,G}}{H_{CO_2}} - C_{CO_2,L} \right) \quad (3)$$

The relationships between the overall coefficients and the individual-phase coefficients can be derived from the two-film theory with an integration of the Henry's law as shown below.

$$\frac{1}{K_G} = \frac{1}{k_G} + \frac{H_{CO_2}}{k_L^o} \quad (4)$$

$$\frac{1}{K_L} = \frac{1}{H_{CO_2} k_G} + \frac{1}{k_L^o} \quad (5)$$

For the Henry's law constant, CO₂ absorption into pure water has been commonly used as the reference system since there is no chemical reaction taking place during mass transfer process. The typical Henry's law equations for pure water were proposed by Versteeg and van Swaaij [3].

$$H_{CO_2,water} = 2.825 \times 10^6 \exp\left(\frac{-2040}{T}\right) \quad (6)$$

where $H_{CO_2,water}$ is the Henry's law constant in $\text{kPa m}^3 \text{ kmol}^{-1}$; T is the system temperature in Kelvin. The Henry's law constant of CO_2 in water can also be calculated from a semi-empirical equation by Harvey where the constant is in unit of pressure. [4] The equation by Harvey shown in Equation (7) is applicable up to 631.7 K.

$$H_{CO_2,water}^\infty = \exp\left[\ln p_{H_2O}^{sat} - 9.4234 \frac{T_c}{T} + 4.0087 \left(1 - \frac{T}{T_c}\right)^{0.355} \frac{T_c}{T} + 10.3199 \exp\left(1 - \frac{T}{T_c}\right) \left(\frac{T}{T_c}\right)^{-0.41}\right] \quad (7)$$

Recently, Equation (7) was modified by Monteiro and Svendsen [5] to Equations (8) and (9) for low pressure (up to 1 MPa) and high pressure (up to 20 MPa) ranges, respectively.

$$H_{CO_2,water}^\infty = \exp\left[\ln p_{H_2O}^{sat} - 7.4455 \frac{T_c}{T} + 3.6456 \left(1 - \frac{T}{T_c}\right)^{0.355} \frac{T_c}{T} + 8.7600 \exp\left(1 - \frac{T}{T_c}\right) \left(\frac{T}{T_c}\right)^{-0.41}\right] \quad (8)$$

$$H_{CO_2,water}^\infty = \exp\left[\ln p_{H_2O}^{sat} - 10.16975 \frac{T_c}{T} + 4.4824 \left(1 - \frac{T}{T_c}\right)^{0.355} \frac{T_c}{T} + 10.6583 \exp\left(1 - \frac{T}{T_c}\right) \left(\frac{T}{T_c}\right)^{-0.41}\right] \quad (9)$$

It should be noted that the Henry's law constant for CO_2 absorption into amine solutions cannot be measured directly as CO_2 undergoes chemical reactions with amine solutions. Based on the fact that N_2O does not react with amines, the so-called N_2O analogy, first introduced by Clarke [6], has been commonly used to estimate the constant of CO_2 in amine solutions. It was assumed that the ratio of CO_2 Henry's constant to N_2O Henry's constant $\left(\frac{H_{CO_2,water}}{H_{N_2O,water}}\right)$ in water is equivalent to the Henry's constant ratio in the amine solution as shown in the following relation [3]:

$$\left(\frac{H_{CO_2,solution}}{H_{N_2O,solution}}\right) = \left(\frac{H_{CO_2,water}}{H_{N_2O,water}}\right) \quad (10)$$

The Henry's law constant for N_2O absorption into pure water can be calculated from the following equations.

Versteeg and van Swaaij, 1988 [3]:

$$H_{N_2O,water} = 8.547 \times 10^6 \exp\left(\frac{-2284}{T}\right) \quad (11)$$

Penttilä et al. 2011 [7]:

$$H_{N_2O,water} = \exp\left(158.245 - 0.00252T - \frac{9048.596}{T} - 20.860 \ln T\right) \quad (12)$$

Similar to the Henry's law constant of CO₂ in water, the Henry's constant of N₂O in water can also be calculated (in pressure unit) from a semi-empirical equations by Monteiro and Svendsen [5] as shown in Equations (13) and (14) for low pressure (up to 1 MPa) and high pressure (up to 20 MPa) ranges, respectively.

$$H_{N_{2O},water}^{\infty} = \exp \left[\ln p_{H_{2O}}^{sat} - 9.9118 \frac{T_c}{T} + 3.2644 \left(1 - \frac{T}{T_c} \right)^{0.355} \frac{T_c}{T} + 11.4552 \exp \left(1 - \frac{T}{T_c} \right) \left(\frac{T}{T_c} \right)^{-0.41} \right] \quad (13)$$

$$H_{N_{2O},water}^{\infty} = \exp \left[\ln p_{H_{2O}}^{sat} - 16.4928 \frac{T_c}{T} + 4.8133 \left(1 - \frac{T}{T_c} \right)^{0.355} \frac{T_c}{T} + 16.3786 \exp \left(1 - \frac{T}{T_c} \right) \left(\frac{T}{T_c} \right)^{-0.41} \right] \quad (14)$$

The Henry's constants of N₂O and CO₂ in various amine solutions reported in the literature are summarized in Table 1.

Table 1. Henry's constant in various amine solutions

Amine system	Temperature (K)	Amine concentration	Data / Equation	Reference
MEA DEA MDEA MEA+MDEA MEA+MDEA DEA+MDEA DEA+MDEA	298	10, 20, 30 wt% 10, 20, 30, 40 wt% 20, 30, 40, 50 wt% 10%MEA/40%MDEA 20%MEA/30%MDEA 10%DEA/40%MDEA 20%DEA/30%MDEA	4299.5 – 7406.3 kPa m ³ kmol ⁻¹ 4548.2 – 8033.2 kPa m ³ kmol ⁻¹ 4845.0 – 9654.9 kPa m ³ kmol ⁻¹ 5679.6 – 9331.6 kPa m ³ kmol ⁻¹ 5464.8 – 8781.5 kPa m ³ kmol ⁻¹ 5544.9 – 7772.9 kPa m ³ kmol ⁻¹ 5501.5 – 7507.4 kPa m ³ kmol ⁻¹ $\log(H) = (h_+ + h_- + h_g)I + \log \left(\sum m_i H_i \right)$	Browning and Weiland, 1994 [8]
MEA, DEA, TEA, DMMEA, MDEA, MIPA, DIPA	298 - 333	Up to 3.0 kmol/m ³ for MEA 3.1 kmol/m ³ for DEA 2.9 kmol/m ³ for TEA 2.4 kmol/m ³ for DMMEA 2.8 kmol/m ³ for MDEA 3.7 kmol/m ³ for MIPA 4.1 kmol/m ³ for DIPA	$H_{N_{2O}} = \frac{1}{(RT)(a_0 + a_1[Amine] + a_2[Amine]^2 + \dots)}$ where $H_{N_{2O}}$ = Henry's constant in kPa m ³ kmol ⁻¹ [Amine] = amine concentration in mol/m ³	Versteeg and van Swaaij, 1988 [3]
MEA DEA DIPA MDEA AMP MEA+MDEA MEA+AMP DEA+MDEA DEA+AMP DIPA+MDEA MDEA+AMP	288-393 288-393 293-333 288-393 289-393 293-393 293-393 293-393 293-393 298 283-333	Up to 36.8 wt% Up to 37.2 wt% Up to 54 wt% Up to 50 wt% Up to 50 wt% 1.5-24%MEA/6-28.5%MDEA 1.5-24%MEA/6-28.5%AMP 1.5-24%DEA/6-47.9%MDEA 1.5-24%DEA/6-28.5%AMP 4.5-10.6%DIPA/6-31.9%MDEA 3.6-41.5%MDEA/0.7-40%AMP	For single amine: $H_{N_{2O},12} = \sum_{i=1}^2 (H_{N_{2O},i} x_i) + A_{12} [x_1 x_2]^2 \left[1 - \frac{T}{B_{12}} \right] \exp[-C_{12} x_2]$ For blended amine: $H_{N_{2O},123} = \sum_{i=1}^3 (H_{N_{2O},i} x_i) + A_{123} \left[x_1 \left(\sum_{i=2}^3 x_i \right) \right]^2 \cdot \left[1 - \frac{T}{B_{123}} \right] \cdot \exp \left[-C_{123} \left(\sum_{i=2}^3 x_i \right) \right] + H_{N_{2O},23}^{EX}$	Penttilä et al., 2011 [7]
DEEA	298, 308, 318, 328, 338	11.82 wt% 23.75 wt% 35.82 wt% 48.16 wt% 61.35 wt% 100 wt%	4257 – 9662 kPa m ³ kmol ⁻¹ 4712 – 8026 kPa m ³ kmol ⁻¹ 4433 – 6398 kPa m ³ kmol ⁻¹ 3666 – 5047 kPa m ³ kmol ⁻¹ 2817 – 3822 kPa m ³ kmol ⁻¹ 957 – 1597 kPa m ³ kmol ⁻¹	Monteiro et al., 2015 [5]
MEA	298-360	10, 20, 30 wt% Up to 0.5 mol/mol CO ₂ loading	$H_{N_{2O},MEA-solution} = \exp \left[(8.3194 + 452 \times 10^{-3}(MEA) - 4.78 \times 10^{-2}(CO_2 Ldg) + 4.56 \times 10^{-2}(MEA)(CO_2 Ldg)) - 1905 \left(\frac{1}{T} - \frac{1}{298.15} \right) \right]$	Dugas and Rochelle, 2011 [9]

LIQUID-SIDE MASS TRANSFER COEFFICIENT

In CO₂ absorption applications, the rate of mass transfer is controlled by mass transfer coefficient in liquid phase. There are three important theories commonly used to describe the phenomenon: i) film theory, ii) penetration theory and iii) surface renewal theory.

Film Theory

The film theory established by Lewis and Whitman [12] is considered to be the oldest and the most obvious picture describing mass transfer in gas-liquid system. The theory is based on the assumption that mass transfer activity takes place by molecular diffusion from gas phase through a stagnant liquid film located at the gas-liquid interface. The diffusion in this case is a steady state process where the concentration profile of the transferred component in the film is linear as shown in Figure 1. In the absence of chemical reaction, the differential equation for steady state mass transfer can be written as:

$$D_{CO_2,L} \frac{\partial^2 C_{CO_2}}{\partial x^2} = 0 \quad (15)$$

where $D_{CO_2,L}$ is the diffusivity of CO₂ in liquid; and x is the distance from the gas-liquid interface. Based on the boundary conditions (at $x = 0$, $C_{CO_2} = C_{CO_2,i}$; at $x =$ film thickness δ , $C_{CO_2} = C_{CO_2,L}$), the mass flux equation can be written as:

$$N_{CO_2} = D_{CO_2,L} \left(\frac{C_{CO_2,i} - C_{CO_2,L}}{\delta} \right) \quad (16)$$

Combining Equations (1) and (16), the mass transfer coefficient without reaction (k_L^o) can be expressed as:

$$k_L^o = \frac{D_{CO_2,L}}{\delta} \quad (17)$$

According to Astarita et al. [13], mass transfer predictions based on the film theory were questionable because the available experimental data on mass transfer coefficient tended to be proportional to the square root of the diffusivity.

Penetration Theory

The penetration theory proposed by Higbie [14] is associated with the motion of liquid elements at the gas-liquid interface as shown in Figure 2. It is assumed that small liquid elements (clusters of liquid molecules) are constantly brought from bulk liquid to the interface, exposed to the gas for a fixed time period (known as contact time t_c), and then swept back to the bulk liquid. Each liquid element at the interface essentially behaves as a

rigid body with no internal motion, allowing mass transfer to take place by molecular diffusion. This transient diffusion is an unsteady state process as the gas-liquid contact time is so short that the concentration gradient of the transferred components within the liquid elements would have no time to develop. The partial differential equation for unsteady CO₂ diffusion to the liquid element can be written as [14]:

$$D_{CO_2,L} \frac{\partial^2 C_{CO_2}}{\partial x^2} = \frac{\partial C_{CO_2}}{\partial t} \tag{18}$$

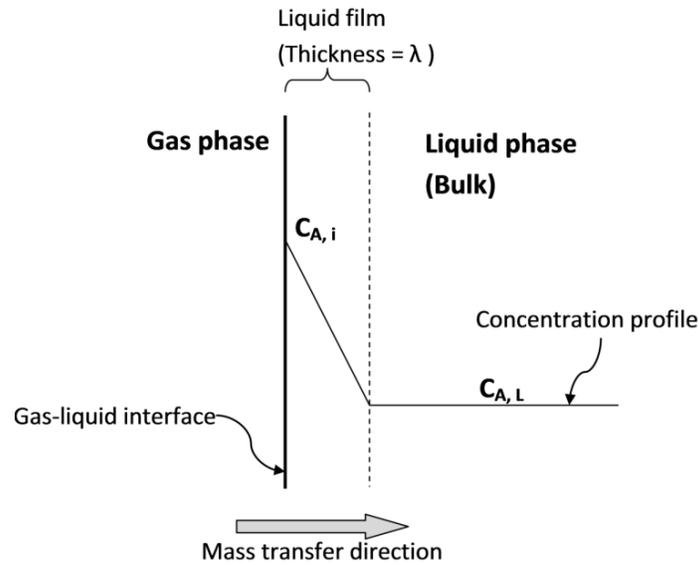


Figure 1. Film theory for mass transfer.

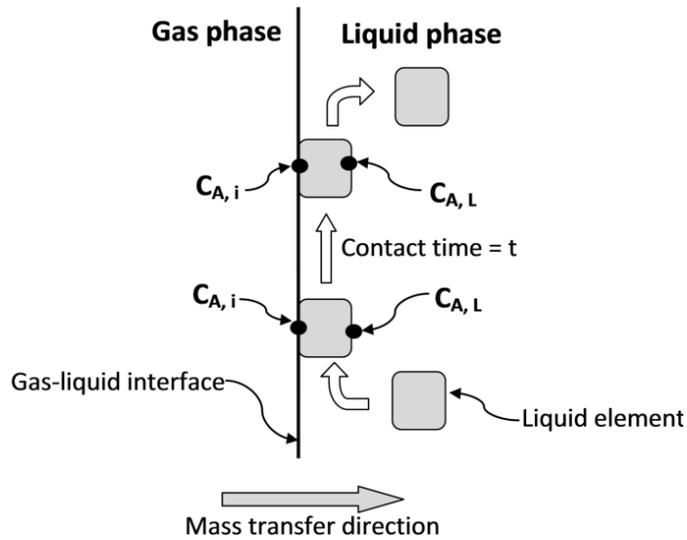


Figure 2. Penetration theory for mass transfer.

It should be noted that all liquid elements are assumed to remain at the interface for the same length of contact time. Based on the boundary conditions i.e., at $t = 0$, $C_{CO_2} = C_{CO_2,L}$ for all distances from the interface, and at $t > 0$, $C_{CO_2} = C_{CO_2,i}$ at the interface, mass transfer coefficient for physical absorption of CO_2 is defined as:

$$k_L^o = 2\sqrt{\frac{D_{CO_2,L}}{\pi t}} \quad (19)$$

The penetration theory has been used extensively in a number of research works since it has been found to accurately represent the diffusion reaction systems. The recent use of the penetration theory is for the interpretation of kinetic data in the single amine systems such as CO_2 -loaded MEA and AHPD as well as blended amine systems such as monoethanolamine (MEA)+2-amino-2-methyl-1-propanol (AMP), piperazine (PZ) + AMP, PZ + methyl diethanolamine (MDEA), and AMP + diethanolamine (DEA) [15-20]. Furthermore, it was also employed in the simulation of CO_2 absorption in packed columns by Khan et al. and Sebastia-Saez et al. [21, 22].

Surface Renewal Theory

Danckwerts proposed in 1951 an extension of the penetration theory known as the surface renewal theory. [23] The theory is based on the assumption that the liquid elements are exposed to the interface for different random periods of time. Distribution of the contact time in this case is characterized by the fraction of liquid surface renewed per unit time (s). This theory is also considered the unsteady state form of mass transfer. The mass transfer coefficient is expressed as:

$$k_L^o = \sqrt{D_{CO_2,L}s} \quad (20)$$

This theory is not as popular as the penetration theory since it requires the information on the rate of surface renewal (s), which is rather difficult to obtain.

Diffusivity of CO_2 in Amine Solution

It is clear from all three theories that diffusivity of CO_2 in liquid phase ($D_{CO_2,L}$) is the essential component for determining the liquid-side mass transfer coefficient. Similar to the Henry's law constant, the diffusivity of CO_2 in amine solution can be estimated by the N_2O analogy presented in the following relation [3]:

$$\left(\frac{D_{CO_2,solution}}{D_{N_2O,solution}}\right) = \left(\frac{D_{CO_2,water}}{D_{N_2O,water}}\right) \quad (21)$$

The diffusivity of CO₂ and N₂O in pure water can be determined from the following equations [3]:

$$D_{CO_2,water} = 2.35 \times 10^{-6} \exp\left(\frac{2119}{T}\right) \quad (22)$$

$$D_{N_2O,water} = 5.07 \times 10^{-6} \exp\left(\frac{2371}{T}\right) \quad (23)$$

The diffusivity of N₂O in amine solutions can be calculated according to the modified Stokes-Einstein relation given below.

$$D_{N_2O,solution} = (D_{N_2O,water}) \left(\frac{\mu_{water}}{\mu_{solution}}\right)^{0.8} \quad (24)$$

where μ_{water} and $\mu_{solution}$ are the viscosity of water and amine solution, respectively. In 2009, Dugas conducted a series of experiments with loaded MEA and PZ solutions and proposed the new relation with viscosity dependence of 0.72 [24].

$$D_{N_2O,solution} = (D_{N_2O,water}) \left(\frac{\mu_{water}}{\mu_{solution}}\right)^{0.72} \quad (25)$$

ROLE OF CHEMICAL REACTIONS ON MASS TRANSFER

Chemical reactions start to play a role in the mass transfer process when a gas stream is brought into contact with a liquid solution containing amine, which can react with the diffusing CO₂. All associated reactions take place only in the liquid side. In general, the chemical reaction influences mass transfer behavior of the system in two ways. First, CO₂ is consumed by chemical reactions in the liquid phase, resulting in a low concentration of CO₂ in the liquid main body ($C_{CO_2,L}$). The driving force for the chemical mass transfer then becomes higher than it would be in the absence of chemical reaction. Second, at a given level of the driving force, the actual rate of mass transfer with chemical reaction may be considerably larger than that without chemical reaction. The ratio of the actual rate with chemical reaction to that which occurs without the reaction under the same driving force is defined as an enhancement factor E [13].

$$E = \frac{k_L}{k_L^0} \geq 1 \quad (26)$$

where k_L is the liquid-side mass transfer coefficient with chemical reaction. Thus, the mass transfer flux of CO₂ can be written as:

$$N_{CO_2} = k_G P (y_{CO_2,G} - y_{CO_2,i}) = E k_L^0 (C_{CO_2,i} - C_{CO_2,L}) \quad (27)$$

with chemical reaction, Equations (4) and (5) can then be respectively rewritten as:

$$\frac{1}{K_G} = \frac{1}{k_G} + \frac{H_{CO_2}}{E k_L^o} \quad (28)$$

$$\frac{1}{K_L} = \frac{1}{H_{CO_2} k_G} + \frac{1}{E k_L^o} \quad (29)$$

To determine the enhancement factor E , several approximate numerical and analytic solutions have been proposed. [2, 13, 25-28] The most commonly used relation is as follows:

$$E = \frac{\sqrt{M \left(\frac{E_\infty - E}{E_\infty - 1} \right)}}{\tanh \sqrt{M \left(\frac{E_\infty - E}{E_\infty - 1} \right)}} \quad (30)$$

where

$$\text{(for penetration theory)} E_\infty = \sqrt{\frac{D_{CO_2,L}}{D_{Amine,L}}} + \sqrt{\frac{D_{Amine,L}}{D_{CO_2,L}}} \left(\frac{C_{Amine}}{z} \right) \left(\frac{H_{CO_2,solution}}{P_{CO_2,i}} \right) \quad (31)$$

$$\text{(for film theory)} E_\infty = 1 + \left(\frac{D_{Amine,L}}{D_{CO_2,L}} \right) \left(\frac{C_{Amine}}{z} \right) \left(\frac{H_{CO_2,solution}}{P_{CO_2,i}} \right) \quad (32)$$

The parameter M can be calculated from Hatta number (Ha) in the following equation:

$$M = Ha^2 \quad (33)$$

where

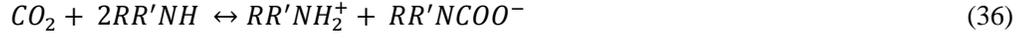
$$Ha = \frac{\sqrt{D_{CO_2,L}(k_{app} + k_{OH^-} C_{OH^-})}}{k_L^o} \quad (34)$$

Note that Equation (34) includes chemical reaction of CO_2 with hydroxyl ion (OH^-), the component commonly found in all aqueous amine solutions. The term k_{OH^-} and C_{OH^-} are the second order rate constant for CO_2-OH^- reaction and concentration of hydroxyl ion, respectively. The k_{app} is the apparent reaction rate constant corresponding to all reactions associated with the CO_2 -amine system, which can be related to the reaction rate and concentration of CO_2 in the following relationship;

$$-r_{CO_2} = k_{app} C_{CO_2} \quad (35)$$

The apparent rate constant can be estimated according to a number of reaction mechanisms. It is commonly known that the chemical reactions for CO_2 absorption into aqueous amine solutions are remarkably complex. According to Astarita et al. [13], the following three main reactions are considered for primary and secondary amines ($RR'NH$).

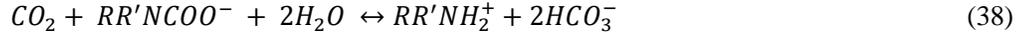
Carbamate formation:



Bicarbonate formation:



Carbamate reversion:

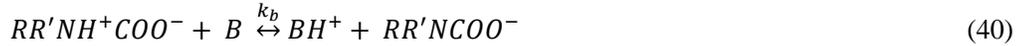


where $RR'NH_2^+$ and $RR'NCOO^-$ are the protonated amine and amine carbamate, respectively.

Table 2. Kinetic correlations for common amines

Amine	correlation	Reference
MEA	$\log(k_2) = 10.99 - \frac{2152}{T}$	Hikita et al., 1977 [30]
AMP	$\log(k_2) = 23.69 - \frac{5176.49}{T}$	Saha et al., 1995 [31]
MDEA	$k_2 = 2.91 \times 10^7 \exp\left(\frac{-2152}{T}\right)$	Rinker et al., 1995 [32]
PZ	$k_2 = 5.8 \times 10^4 \exp\left(\frac{-3.5 \times 10^4}{R} \left(\frac{1}{T} - \frac{1}{298}\right)\right)$	Samanta and Bandyopadhyay, 2007 [33]
AHPD	$k_2 = 5.08 \times 10^{11} \exp\left(\frac{-6465}{T}\right)$	Bougie and Iliuta, 2009 [16]
DEAB	$k_2 = 4.01 \times 10^{13} \exp\left(\frac{-7527.7}{T}\right)$	Sema et al., 2012 [34]
OH ⁻	$\log(k_2) = 13.635 - \frac{2895}{T}$	Pinsent et al., 1956; Danckwerts and Sharma, 1966 [35-36]

In general, the carbamate formation predominates when the CO₂ loading in amine solution is less than 0.5 mol CO₂/mol amine, and the carbamate reversion plays a major role when the CO₂ loading exceeds 0.5 mol CO₂/mol amine. The carbamate formation is made up of two steps commonly referred to as zwitterions mechanism [29]:

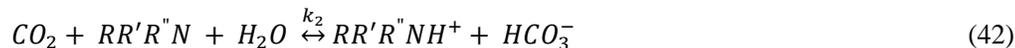


where B represents base species that could be either amine ($RR'NH$), hydroxyl ion (OH^-) or water (H_2O). With the above mechanism, the apparent rate constant for primary and secondary amines can be written as:

$$k_{app} = \frac{k_2 C_{Amine}}{\left(1 + \frac{k_{-1}}{\sum_i (k_{b,i} C_{B,i})}\right)} \quad (41)$$

Equation (41) has been commonly used for analyzing kinetics data for MEA, DEA, DIPA, PZ and AHPD.

For tertiary and hindered amines such as MDEA, AMP, and DEAB, the reaction mechanism is simpler. Bicarbonate formation is considered to be the primary reaction.



The apparent rate constant in this case can be written as:

$$k_{app} = k_2 C_{Amine} \quad (43)$$

Based on the above equation, the second order rate constant (k_2) is the crucial parameter for estimating the enhancement factor E . Table 2 summarizes kinetic correlations developed for a number of common amines.

ROLE OF VAPOR-LIQUID-EQUILIBRIUM ON MASS TRANSFER

The relationship between CO₂ content in an amine solution and CO₂ partial pressure in the gas phase under equilibrium conditions is one of the most important information required for the design of a CO₂ absorption unit. This vapor-liquid-equilibrium establishes the CO₂ concentration gradient between the two fluids, driving mass transfer process to occur. For a gas absorption application, it is common to represent mass transfer driving force in terms of pressure gradient. Therefore, mass flux for CO₂ absorption into amine solution can also be written as:

$$N_{CO_2} = K_G(P_{CO_2,G} - P_{CO_2,L}^*) \quad (44)$$

where $P_{CO_2,G}$ is the CO₂ partial pressure in the gas phase, and $P_{CO_2,L}^*$ is the CO₂ partial pressure in equilibrium with the content of CO₂ in amine solution. To allow the CO₂ absorption into the amine solution, the gas-phase CO₂ partial pressure must be greater than the corresponding equilibrium $P_{CO_2,L}^*$.

The equilibrium data for CO₂-amine system are available and presented in terms of “CO₂ loading” (in a unit of mole CO₂ per mole amine) representing the relationship between gas-phase CO₂ partial pressure and CO₂ content of amine solution. Such equilibrium data have been reported for decades as a function of temperature, type of amine used, and concentration of amine. A comprehensive data collection for common amines such as MEA, DEA, DIPA, MDEA, AMP, and their blends can be found in the book by Kohl and Nielsen [37]. The equilibrium data for newly developed amines can also be found in recent literature. It should be noted that, for the CO₂ absorption from a low pressure flue gas, CO₂ partial pressure in the gas phase is kept below atmospheric pressure (e.g., 101.3 kPa). Figure 3 shows a summary of equilibrium data applicable to flue gas conditions.

For the design and operation of CO₂ absorption columns, the equilibrium data are used in combination with the operating data commonly known as “operating line.” This operating

line represents a relationship between partial pressure of CO₂ in the gas stream and CO₂ content in the amine solution that is derived directly from material balance around the absorption column. Figure 4 shows a schematic diagram of a packed absorption column in which the entire height is divided into a series of sections with a differential height of dz .

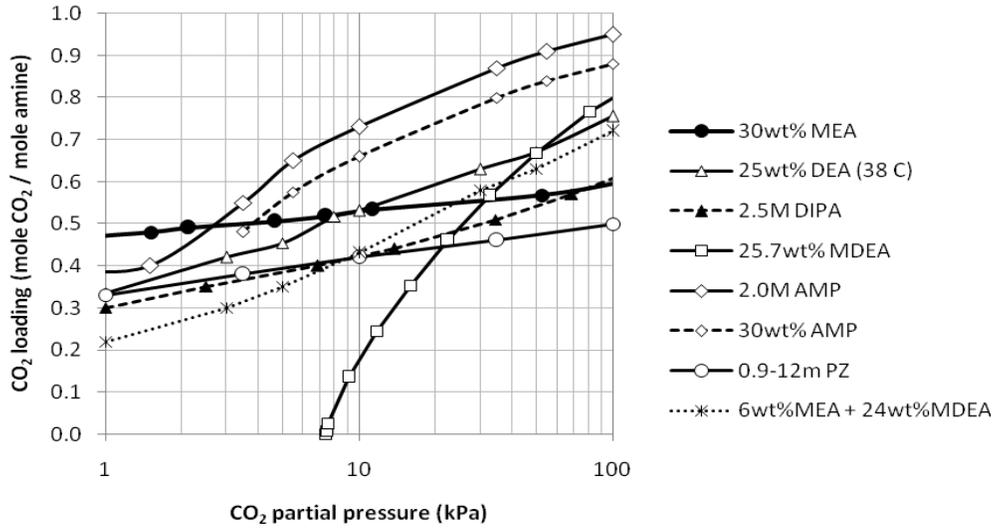


Figure 3. Equilibrium data for CO₂-amine system at 40°C.

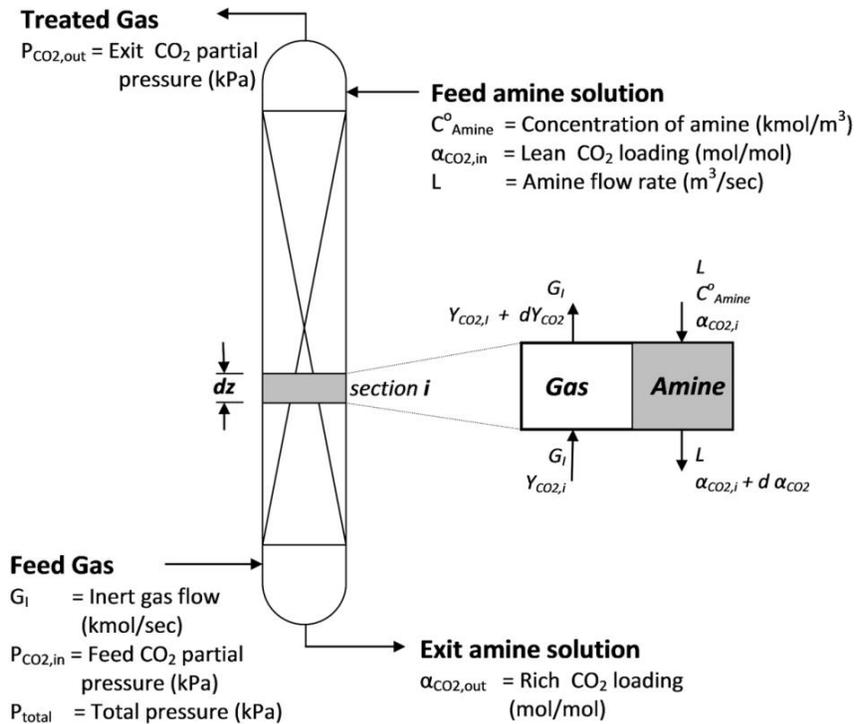


Figure 4. Schematic diagram of a packed column.

For each column section, the amount of CO₂ removed from the gas phase is equivalent to the amount of CO₂ absorbed into the amine solution. Therefore, the material balance of CO₂ can be written as:

$$G_I(dY_{CO_2}) = G_I d\left(\frac{P_{CO_2}}{P_{total}-P_{CO_2}}\right) = LC_{Amine}^o(d\alpha_{CO_2}) \quad (45)$$

where Y_{CO_2} is the mole ratio of CO₂ in the gas phase. The material balance equation can also be rewritten as:

$$\frac{dP_{CO_2}}{d\alpha_{CO_2}} = \left\{ \frac{(P_{total}-P_{CO_2})^2}{P_{total}} \right\} \left(\frac{L}{G_I} \right) C_{Amine}^o \quad (46)$$

with complete information on process parameters (including gas flow rate, liquid flow rate, amine concentration, CO₂ content in feed gas, and CO₂ loading of lean amine solution), the operating line for CO₂ absorption column can be drawn as illustrated in Figure 4 for a CO₂-MEA system.

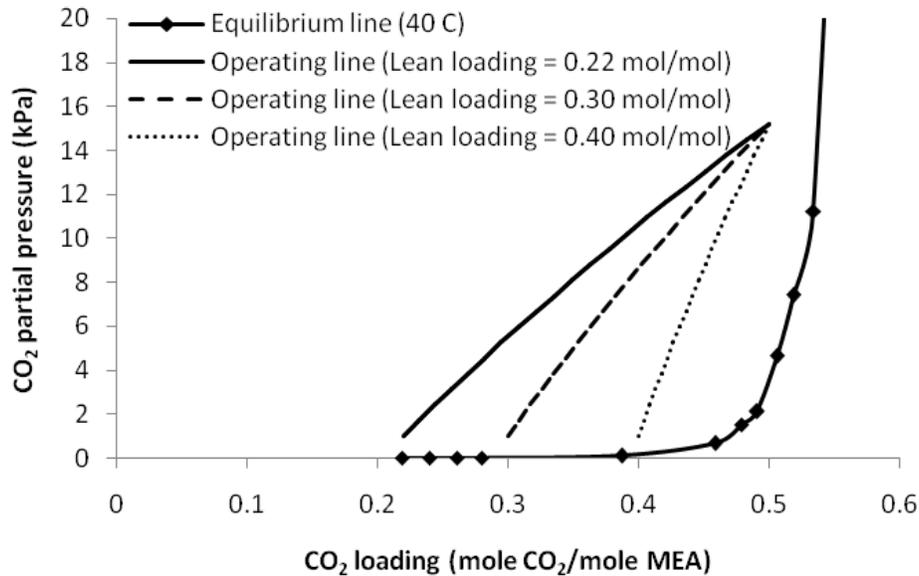


Figure 5. Equilibrium and operating lines of CO₂ absorption column using 30wt% MEA solution ($P_{CO_2,in} = 15$ kPa and $P_{CO_2,out} = 1$ kPa).

It should be noted that the CO₂ absorption into the amine solution can be achieved only when the operating line is located above the equilibrium line. From a thermodynamic viewpoint, the greater the proximity between the operating and the equilibrium lines, the higher the mass transfer driving force established within the absorption column. From Figure 5, a larger driving force can be achieved by using the lean amine solution with a lower CO₂ loading (0.22 mol/mol in this case). Producing the lean amine solution, however, requires a considerable amount of energy during solvent regeneration process, thus leading to more operating cost for capturing CO₂. The use of the relatively higher lean CO₂ loading for the

absorption column is now considered as one of the operational strategies to reduce energy consumption of the entire CO₂ capture unit. Increasing the lean loading, however, must be done within thermodynamic limits controlled by the equilibrium lines for individual amine solutions. Table 3 shows the maximum levels of lean CO₂ loading for selected amine solutions according to their equilibrium data at 40°C.

Table 3. Maximum lean CO₂ loading for amine solutions at 40°C

Amine solution	Max. lean CO ₂ loading (mol/mol)
30 wt% MEA	0.46
25wt% DEA	0.33
2 kmol/m ³ AMP	0.37
PZ	0.32
26 wt% MDEA	Not applicable

HEAT OF REACTION BETWEEN CO₂ AND AMINE

As mentioned in the previous section, the absorption of CO₂ into aqueous amine solutions is associated with a series of chemical reactions such as carbamate formation and bicarbonate formation. These chemical reactions are exothermic, that release a certain amount of heat energy to the surroundings, resulting in an increase in temperature of the medium in which the reactions are taking place. In the typical operation, absorption reactions occur in a full-length absorption column where the amine solution with a relatively low temperature is introduced into the column top, absorbs CO₂ from the gas stream while trickling down through column internals, and finally reaches the column bottom. Because of the exothermic nature of the CO₂ absorption, the operation of industrial columns never takes place at a constant and specific temperature, but is always subjected to significant dynamic variations in temperature throughout the column length. Such exothermic effect can be observed from the temperature bulk commonly developed near the bottom of the absorption column.

The system temperature is thus one of the most important process parameters controlling all fundamental aspects of gas absorption including mass transfer (diffusion), kinetics, as well as vapor-liquid equilibrium or thermodynamics. Knowing the magnitude of heat released due to absorption reactions (commonly known as heat of reaction or enthalpy of solution) can help us determine energy balance and temperature profiles around the absorption column. In addition, the use of heat of reaction data is also necessary for the design and operation of amine regeneration column as it helps us evaluate energy consumption (or heat duty) for the entire CO₂ absorption plant.

Because of the recent focus on the development of cost-effective and energy-efficient carbon capture technologies, the heat of reaction between CO₂ and amine has become one of the most studied research topics in the last decade. To date, there are a number of research studies reporting heat of reaction data for different amines including conventional amines such as MEA, DEA, and MDEA, the sterically hindered amine such as AMP, and the polyamine such as PZ. The reported values of heat of reaction were obtained either through the estimation using vapor-liquid equilibrium (VLE) data, or through the direct measurement using different types of calorimeters. The latter appears to be the common trend for more

recent studies. In general, each amine has its own range of heat of reaction that would not be affected by amine concentration, but in most cases varies significantly with CO₂ loading of amine solution. For the effect of temperature, it was found to be inconclusive as some researchers reported the increase in heat of reaction with temperature while some other researchers demonstrated no temperature impact. A summary of heat of reaction data for well recognized amines is given below.

Conventional Amine

MEA is the conventional amine that has been most referred to in many studies as the baseline/benchmark solvent for the development of cost-effective carbon capture technologies. The information on reaction heat for CO₂ into MEA solution was reported as early as 1974 by Lee [38] and has been published more intensively in recent years [39-42]. Most published data were presented in terms of differential heat of reaction (ΔH_{diff}) representing heat release per mole of CO₂ when a small amount of CO₂ is absorbed by the solution at a specific CO₂ loading.

The effects of process parameters on heat of reaction have been studied to understand synergistic behavior of energy requirement for plant operation. It was found that heat of reaction for MEA typically remains unchanged at 85 kJ/mol of CO₂ (approximately 1,930 kJ/kg CO₂) with CO₂ loading of solution. However, it decreases with an increase in CO₂ loading when the CO₂ loading is raised beyond its theoretical limit (0.50 mol CO₂/mol amine) [37]. For instance, the reaction heat value decreases to 70 and 50 kJ/mol of CO₂ when the CO₂ loading is increased to 0.53 and 0.60 mol CO₂/mol amine, respectively. Such CO₂ loading effect on heat of the reaction was consistently confirmed by a number of studies [38, 41-42].

The effect of temperature was mentioned in the study by Kim [41] where the differential heat of reaction of 30 wt% MEA solution was measured experimentally in a calorimeter at 40°C, 80°C, and 120°C. It was found that the heat of reaction increases with absorption temperature. The similar temperature effect was also addressed in a work by Mathonat [39]. In contrast, other studies including Lee et al. and Arcis et al. [38, 42] found conflicting findings in that the temperature has no effect on heat of reaction.

The effect of amine concentration was studied by Carson et al. [40] and by Arcis et al. [42]. They found that amine concentration has no significant impact on heat of reaction for the MEA solution with concentrations ranging from 10 to 30 wt%.

MDEA is another important conventional amine commonly referred to in many carbon capture studies. Its relatively low heat of reaction with CO₂ makes this tertiary amine popular as one of the key ingredients in several amine blends such as MEA-MDEA, AMP-MDEA, and PZ-MDEA. Similar to the CO₂ loading effect found in MEA systems, the heat of reaction for MDEA solution remains constant at 62 kJ/mole of CO₂ (approximately 1,409 kJ/kg CO₂) for the CO₂ loading up to 0.1 mol CO₂/mol amine [37]. It, however, gradually decreases to 54.3 and 33.7 kJ/mol of CO₂ as the CO₂ loading increases to 0.5 and 1.0 mol CO₂/mole amine, respectively. Most studies [43-45] reported that heat of reaction for MDEA tends to increase with temperature, except for the study by Kabadi suggesting no temperature effect [46]. Increasing MDEA concentration was reported to cause heat of reaction to rise [43, 45, 47].

DEA is the secondary amine that reacts with CO₂ at a lower rate compared to MEA but a much higher rate compared to MDEA. Similarly, the heat of reaction of DEA is also in between those of these two amines. For a DEA solution (3.5-N), the differential heat of reaction is at 76.3 kJ/mol of CO₂ (approximately 1,734 kJ/kg CO₂) for the CO₂ loading of 0.2 mol CO₂/mol amine. It can be reduced to 65.4 and 50.3 kJ/mol of CO₂ as the CO₂ loading reaches 0.4 and 0.5 mol CO₂/mol amine.

Hindered Amine and Polyamines

AMP is the most studied sterically hindered amine for CO₂ absorption as it offers higher CO₂ absorption capacity (i.e., 1.0 mol CO₂/mol amine) and lower heat of reaction compared to MEA. According to Chowdhury et al. [48], the heat of reaction for AMP is about 76 kJ/mol of CO₂ accounting for 12% lower than that of MEA. Despite the great attention received, data on the heat of reaction for AMP is scarce. Arcis [49] reported the differential heat of reaction measured experimentally for 15 and 30 wt% aqueous AMP at 49.35°C and pressure up to 5 MPa.

PZ is a polyamine that has been studied extensively in recent years. This polyamine was primarily used as a promoter with other amines to improve the overall CO₂ absorption rate. The concentrated aqueous PZ solution alone is recently considered as a potential candidate for capturing CO₂ from coal-fired power stations [50]. Heat of CO₂ absorption with aqueous PZ was measured by Hilliard and Liu using ChemiSens CPA-122 reaction calorimeter [51].

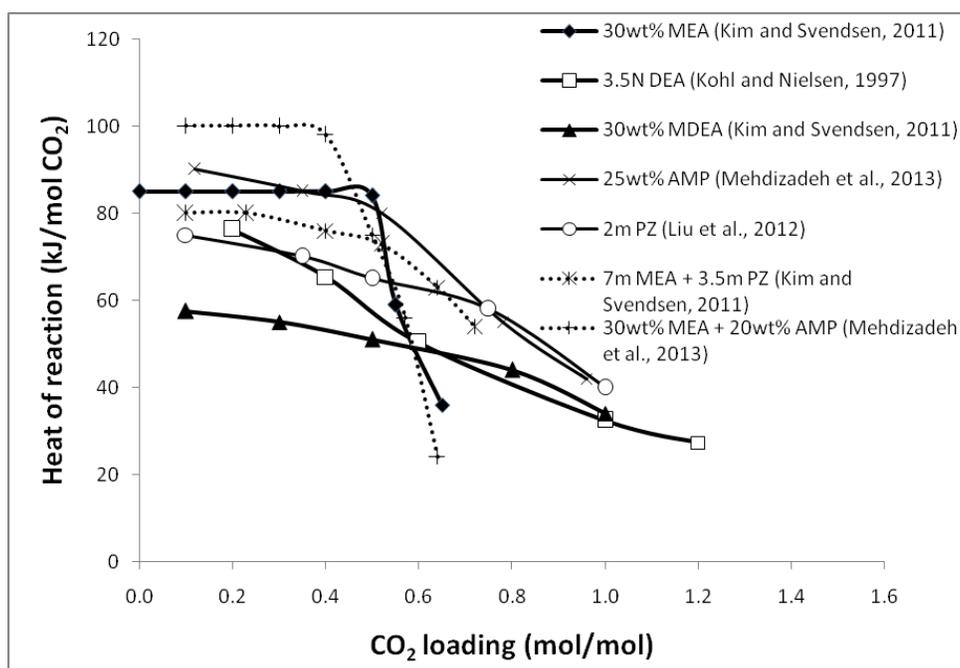


Figure 6. Heat of reaction for different amines. Data from references [37, 52-53].

In addition to PZ, heat of reaction of other polyamines including diethylenetriamine (DETA), triethylenetetramine (TETA), tetraethylenepentamine (TEPA) and (MAPA) was also measured in recent years. Based on the comparison study by Kim [52], the values of heat of reaction are 87.00, 89.48, 84.91, and 85.87 kJ/mol of CO₂ for MAPA, DETA, TETA, and TEPA respectively. These are comparable to that of conventional MEA.

Also, several synthetic amines (recently developed by the Research Institute of Innovative Technology for the Earth-RITE) were tested for their heat of reaction with CO₂ [48]. It was found that the four synthetic amines referred to as IPEA, IPAP, IBAE, and SBAE offer lower heat of reaction compared to the MEA, ranging from 61 to 69 kJ/mol of CO₂. For comparison purposes, values of the heat of reaction for different amines are summarized in Figure 6.

SIMULATION OF ABSORPTION COLUMN

From a practical aspect, the CO₂ absorption operation is commonly carried out in a gas-liquid contactor where the gas stream containing CO₂ is brought into a direct contact with the amine solution. The typical contactor is the packed column fitted with packing materials that could be categorized as random and structured packings. With its excellent performance and advanced design, the structured packing has become the most studied column internal for CO₂ capture application.

To design the CO₂ absorption unit such that a desired capture target is met, mass transfer performance of the full-length absorption column must be precisely known. Simulating the column performance for CO₂ absorption by amine is not an easy task due to the fact that all mass-transfer and heat-transfer activities (including molecular diffusion, CO₂-amine reaction, vapor-liquid equilibrium, and heat generation by exothermic reaction) take place simultaneously. The most common simulation strategy is based on the theoretical packed column design procedure for adiabatic gas absorption with chemical reaction, which was first described by Pandya [54]. The procedure accounts for heat of absorption, solvent evaporation and condensation, chemical reaction in liquid phase, and heat-and mass-transfer resistance in both gas and liquid phases. In addition, the hydrodynamic features of the packed column revealing an interfacial gas-liquid contact area must also be included in the simulation procedure.

The simulation of an absorption column is achieved by dividing the column height into a series of sections with a differential height of dz as illustrated previously in Figure 2. Each of these sections is treated as a non-equilibrium (or rate-based) discrete stage, which is governed by material balance and energy balance equations. For material balance, the amount of CO₂ removed from the gas phase is equivalent to the amount of CO₂ absorbed into the amine solution as shown below.

$$G_I \left(\frac{dY_{CO_2}}{dz} \right) = -LC_{Amine}^o \left(\frac{d\alpha_{CO_2}}{dz} \right) \quad (47)$$

where G_I is the inert gas flow rate, Y_{CO_2} is the mole ratio of CO₂ in gas phase, z is the column length, L is the liquid flow rate, C_{amine}^o is the total amine concentration, and α_{CO_2} is the CO₂ loading in solution.

For the energy balance, the change in sensible heat of the amine solution (liquid phase) is derived from three energy components including: i) sensible heat of the gas phase, ii) condensation or evaporation of water vapor in the gas phase, and iii) heat of reaction between CO₂ and amine due to absorption activities. The energy balance equation can be written as:

$$LC_{p,L} \left(\frac{dT_L}{dz} \right) = G_I (\sum_j Y_j C_{p,j}) \left(\frac{dT_G}{dz} \right) + G_I \lambda_{water} \left(\frac{dY_{water}}{dz} \right) + G_I H_{rx} \left(\frac{dY_{CO_2}}{dz} \right) \quad (48)$$

where T_L and T_G are the temperature of amine solution and gas stream, respectively, $C_{p,L}$ and $C_{p,j}$ are the specific heat of the amine solution and gaseous component j , respectively, Y_j is the mole ratio of component j in gas phase, λ_{water} is the heat of vaporization for water, and H_{rx} is the heat of reaction between CO₂ and amine. Besides the balance equations, the column sections are also governed by mass-transfer and energy transfer equations. Mass transfer of CO₂ from gas to liquid phases can be written as:

$$G_I \left(\frac{dY_{CO_2}}{dz} \right) = k_{G,CO_2} P a_e (y_{CO_2,G} - y_{CO_2,i}) = Ek_L^o a_e \left(\frac{Py_{CO_2,i}}{H_{CO_2}} - C_{CO_2,L} \right) \quad (49)$$

where k_{G,CO_2} is the gas-phase mass transfer coefficient for CO₂, and a_e is the effective mass-transfer area provided by the column internals. A similar mass transfer equation can also be written for water vapor in the gas phase.

$$G_I \left(\frac{dY_{water}}{dz} \right) = k_{G,water} P a_e (y_{water,G} - y_{water,i}) \quad (50)$$

The energy transfer rate between gas and liquid phases can be described below.

$$G_I (\sum_j Y_j C_{p,j}) \left(\frac{dT_G}{dz} \right) = h_G a_e [T_G - T_L] \quad (51)$$

where h_G is the gas-phase heat transfer coefficient. It should be noted that the effective area a_e can be determined using equations developed specifically for certain column internals or packings.

It is obvious from the above material and energy equations that the column simulation requires not only the information on properties of amine used for CO₂ capture, but also the operational data and design specifications of the carbon capture process. Henry's law constant (H_{CO_2}) and vapor-liquid equilibrium data (or CO₂ solubility data) are used for establishing the driving-force in mass-transfer equation for CO₂. Diffusivity of CO₂ (D_{CO_2}) and rate constant of CO₂-amine reaction (k_2 or k_{app}) are used to determine the enhancement factor (E) and mass-transfer coefficient (k_L^o) in the CO₂ mass-transfer equation. Heat of reaction is the key component in the energy balance equation defining the changes in fluid temperature along the length of the absorption column (dT_L/dz and dT_G/dz). The operating conditions such as operating pressure (P), gas flow rate (G_I), liquid flow rate (L), and total amine concentration (C^o_{Amine}) are used in both balance and transfer equations. The concentrations of CO₂ in the feed gas entering the column and in the treated gas leaving the column are design specifications defining the boundaries or scope of the column simulation.

The simulation of the absorption column is an iterative procedure where the calculations for individual non-equilibrium stages (based on above equations) are carried out repeatedly

until all boundary conditions of the column are satisfied. The following describes one possible algorithm that starts (for a given iteration) the calculations for the first non-equilibrium stage located at the bottom of the absorption column where the gas stream is introduced. For this first stage, the calculations are based on operating conditions of feed gas (i.e., composition, temperature and flow rate) as well as the assumed conditions of rich amine solution (i.e., CO₂ loading and temperature). The calculation results from the first non-equilibrium stage serve as the input data for the calculations in the adjacent stage. The stage calculations are carried out sequentially from the bottom to the top where the treated gas stream leaves the absorption column. The calculation results from the top stage are then compared to the design specification which could be either the height of the column or the concentration of CO₂ required in the treated gas. If the required specifications are satisfied, the simulation calculations are terminated and the complete results are produced. Otherwise, the sequential calculations will be repeated using new assumed conditions of the rich amine solution leaving the bottom of the column. The followings are the general calculation steps carried out for individual stages;

- Calculations of fluid physical properties such as density, viscosity, surface tension, and specific heat.
- Calculations of effective mass-transfer area (a_c).
- Calculations of fundamental data including diffusivity, Henry's constant, rate constant, enhancement factor, vapor-liquid equilibrium (or CO₂ solubility), and heat of reaction.
- Calculations of mass-transfer and heat-transfer coefficients.
- Calculations of changes in temperature and composition of gas- and liquid-phases within the current non-equilibrium stage.
- Calculations of input conditions for the next non-equilibrium stage.

In general, the simulation results from the full-length absorption column are presented as a gas-phase CO₂ concentration profile, CO₂ loading profile for the amine solution and temperature profiles for both gas- and liquid-phases. The profiles are usually plotted against the axial positions along the column. To validate the simulation accuracy, the profiles are compared with the experimental results or measured data obtained from the CO₂ capture plants or pilot-plants.

Figure 7 shows examples of simulation results presented as the temperature profiles along the absorption column. The temperature bulge near the bottom of the column is caused by the heat transfer between the incoming gas stream with a relatively low temperature and the warmer amine solution leaving the column after absorbing CO₂. The figure also shows the good agreement between the simulation data and the experimental results. It should be noted that the experimental results were taken from the published pilot plant data [61] obtained from the Technical University of Denmark. The pilot plant was equipped with 0.1m-diameter absorption column packed with Mellapak 250Y structured packing. The packing height of the column can be varied up to 8.2 m. The tested data were obtained for the CO₂ absorption into 30 wt% MEA aqueous solution using the gas stream containing about 9.2-10.5% CO₂. Figure 7-a and -b show the temperature profiles when a lean CO₂ loading of 0.112 mol/mol was used, while Figure 7-c shows the profiles for the lean CO₂ loading of 0.271 mol/mol.

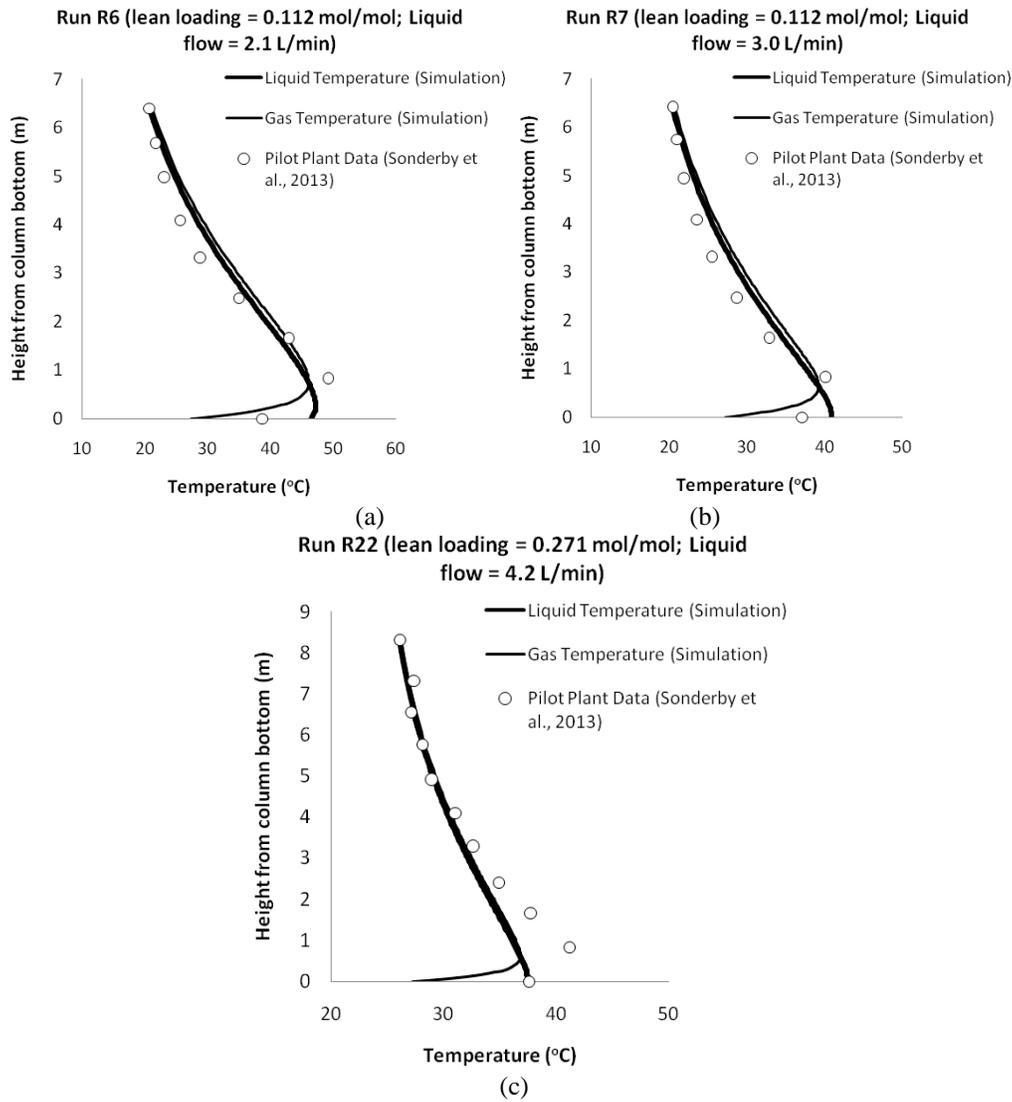


Figure 7. Simulated temperature profiles of CO₂ absorption column using MEA solution.

CONCLUSION

Mass transfer in CO₂ absorption processes is a complex mechanism that depends heavily on a series of fundamental attributes of liquid absorbents and gas-liquid contactors including chemical reaction kinetics, vapor-liquid equilibrium, heat transfer and hydrodynamics. Because of their interrelated nature, all of these attributes must be included in any comprehensive column model to reveal the practicality of absorption system. In other words, proper use of mass transfer knowledge in the column design serves as a powerful tool to evaluate if the currently available or the newly developed solvents can practically be used within the design limit of industrial equipments to achieve a required CO₂ capture target.

This book chapter describes the application of mass transfer knowledge to the design of CO₂ absorption columns using amine as liquid absorbent, which is considered the most mature technology for capturing CO₂ from low-pressure gas stream. A wealth of data, such as mass-transfer coefficient, Henry's law constants, equilibrium solubility of CO₂, reaction kinetics, and physical properties are presently available for the conventional amines, particularly MEA. With such data, it is apparent that capturing CO₂ using aqueous amine solutions is achievable by using absorption columns with reasonable sizes, and the amine-based technology has a promise for future industrial use despite its shortcoming including intensive energy consumption, generation of degradation products, and amine emission due to volatility. Today, a series of newly developed solvents for CO₂ absorption processes are being studied at research stage. Examples of these are ionic-liquid and ionic-liquid based solvents. They are known to have merits on being environmentally friendly and consuming less energy for solvent regeneration, and demerits on low absorption performance compared to amines. Thus, to compete with amines, mass transfer performance of these solvents must be improved significantly. However, the mass transfer data for these newly developed solvents are limited. There is still a vast research opportunity in this area.

REFERENCES

- [1] Treybal, R. E. *Mass-Transfer Operations*, 3rd ed.; McGraw-Hill: Singapore, 1980.
- [2] Perry, R. H.; Green, D. *Perry's Chemical Engineers' Handbook*, 6th ed; McGraw-Hill Book Company: New York, 1984.
- [3] Versteeg, G. F.; van Swaaij, W. P. M., (1988). Solubility and Diffusivity of Acid Gases (CO₂; N₂O) in Aqueous Alkanolamine Solutions. *J. Chem. Eng. Data*. 33, 29–34.
- [4] Harvey, A. H. Semiempirical Correlation for Henry's Constants over Large Temperature Ranges. *AIChEJ*. 1996, 42, 1491–1494.
- [5] Monteiro, J. G. M. S.; Svendsen, H. F., (2015). The N₂O Analogy in the CO₂ Capture Context: Literature Review and Thermodynamic Modeling Considerations. *Chem. Eng. Sci.* 126, 455-470.
- [6] Clarke, J. K. A., (1964). Kinetics of Absorption of Carbon Dioxide in Monoethanolamine Solutions at Short Contact Times. *Ind. Eng. Chem. Fundam.* 3(3), 239-245.
- [7] Penttilä, A.; Dell'Era, C.; Uusi-Kyyny, P.; Alopaeus, V., (2011). The Henry's Law Constant of N₂O and CO₂ in Aqueous Binary and Ternary Amine Solutions (MEA, DEA, DIPA, MDEA, and AMP). *Fluid Phase Equilib.* 311, 59–66.
- [8] Browning, G. J.; Weiland, R. H., (1994). Physical Solubility of Carbon Dioxide in Aqueous Alkanolamines via Nitrous Oxide Analogy. *J. Chem. Eng. Data*. 39, 817–822.
- [9] Dugas, R. E.; Rochelle, G. T., (2011). Modeling CO₂ Absorption into Concentrated Aqueous Monoethanolamine and Piperazine. *Chem. Eng. Sci.* 66, 5212-5218.
- [10] Yoon, J. H.; Baek, J. I.; Yamamoto, Y.; Komai, T.; Kawamura, T., (2003). Kinetics of Removal of Carbon Dioxide by Aqueous 2-Amino-2-Methyl-1,3-Propanediol. *Chem. Eng. Sci.* 58, 5229-5237.

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- [11] Ma'mun, S.; Svendsen, H. F., (2009). Solubility of N₂O in Aqueous Monoethanolamine and 2-(2-Aminoethyl-Amino) Ethanol Solutions from 298 to 343K. *Energy Procedia*. 1, 837-843.
- [12] Lewis, W. K.; Whitman, W. G., (2015). Principles of Gas Absorption. *Ind. Eng. Chem.* 1924, 16(12).
- [13] Astarita, G.; Savage, D. W.; Bisio, A. *Gas Treating with Chemical Solvents*; John Wiley and Sons: New York, 1983.
- [14] Higbie, R., (1935). The Rate of Absorption of a Pure Gas into a Still Liquid During Short Periods of Exposure. *Trans. Am. I. Chem. Eng.* 31, 365-389.
- [15] Putta, K. R.; Knuutila, H.; Svendsen, H. F., (2014). Activity Based Kinetics and Mass Transfer of CO₂ Absorption into MEA Using Penetration Theory. *Energy Procedia*. 63, 1196 – 1205.
- [16] Bougie, F.; Iliuta, M. C., (2009). Kinetics of Absorption of Carbon Dioxide into Aqueous Solutions of 2-Amino-2-Hydroxymethyl-1,3-Propanediol. *Chem. Eng. Sci.* 64, 153 – 162.
- [17] Luo, X.; Hartono, A.; Hussain, S.; Svendsen, H., (2015). Mass Transfer and Kinetics of Carbon Dioxide Absorption into Loaded Aqueous Monoethanolamine Solutions. *Chem. Eng. Sci.* 123, 57–69.
- [18] Mandal, B. P.; Guha, M.; Biswas, A. K.; Bandyopadhyay, S. S., (2001). Removal of Carbon Dioxide by Absorption in Mixed Amines: Modeling of Absorption in Aqueous MDEA/MEA and AMP/MEA Solutions. *Chem. Eng. Sci.* 56, 6217–6224.
- [19] Dash, S. K.; Samanta, A.; Samanta, A. N.; Bandyopadhyay, S. S., (2011). Absorption of Carbon Dioxide in Piperazine Activated Concentrated Aqueous 2-Amino-2-Methyl-1-Propanol Solvent. *Chem. Eng. Sci.* 66, 3223–3233.
- [20] Samanta, A.; Bandyopadhyay, S. S., (2011). Absorption of Carbon Dioxide into Piperazine Activated Aqueous N-Methyldiethanolamine. *Chem. Eng. J.* 171, 734– 741.
- [21] Khan, F. M.; Krishnamoorthi, V.; Mahmud, T., (2011). Modelling Reactive Absorption of CO₂ in Packed Columns for Post-Combustion Carbon Capture Applications. *Chem. Eng. Res. Des.* 89, 1600–1608.
- [22] Sebastia-Saez, D.; Gua, S.; Ranganathan, P.; Papadikis, K., (2015). Micro-Scale CFD Modeling of Reactive Mass Transfer in Falling Liquid Films within Structured Packing Materials. *Int. J. Greenh. Gas Control.* 33, 40–50.
- [23] Danckwerts, P. V., (1951). Significance of Liquid-Film Coefficients in Gas Absorption. *Ind. Eng. Chem.* 43(6), 1460.
- [24] Dugas, R. E. *Carbon Dioxide Absorption, Desorption and Diffusion in Aqueous Piperazine and Monoethanolamine*. Ph.D. Dissertation. University of Texas at Austin, 2009.
- [25] Rase, H. F. *Chemical Reaction Design for Process Plants: Volume 1-Principles and Techniques*; John Wiley and Sons: New York, 1977.
- [26] deCoursey, W. J., (1982). Enhancement Factors for Gas Absorption with Reversible Reaction. *Chem. Eng. Sci.* 37(10), 1483-1489.
- [27] deCoursey, W. J.; Thring, R. W., (1989). Effects of Unequal Diffusivities on Enhancement Factors for Reversible and Irreversible Reaction. *Chem. Eng. Sci.* 44(8), 1715-1721.

- [28] Winkelman, J. G. M.; Brodsky, S. J.; Beenackers, A. A. C. M., (1992). Effects of Unequal Diffusivities on Enhancement Factors for Reversible Reaction: Numerical Solutions and Comparison with deCoursey's Method. *Chem. Eng. Sci.* 47(2), 485-489.
- [29] Caplow, M., (1968). Kinetics of Carbamate Formation and Breakdown. *J. Am. Chem. Soc.* 90, 6795-6803.
- [30] Hikita, H.; Asai, S.; Ishikawa, H.; Honda, M., (1977). Kinetics of Reactions of Carbon Dioxide with Monorthanolamine, Diethanolamine and Triethanolamine by a Rapid Mixing Method. *Chem. Eng. J.* 13, 7-12.
- [31] Saha, A. K.; Bandyopadhyay, S. S., (1995). Kinetics of Absorption of CO₂ into Aqueous Solutions of 2-Amino-2-methyl-1-propanol. *Chem. Eng. Sci.* 50(2), 3587-3598.
- [32] Rinker, E. B.; Ashour, S. S.; Sandall, O. C., (1995). Kinetics and Modelling of Carbon Dioxide Absorption into Aqueous Solutions of N-methyldiethanolamine. *Chem. Eng. Sci.* 50, 755-768.
- [33] Samanta, A.; Bandyopadhyay, S. S., (2007). Kinetics of and Modelling of Carbon Dioxide Absorption into Aqueous Solutions of Piperazine. *Chem. Eng. Sci.* 62, 7312-7319.
- [34] Sema, T.; Naami, A.; Liang, Z.; Idem, R.; Tontiwachwuthikul, P.; Shi, H.; Wattanapan, P.; Henni, A., (2012). Analysis of Reaction Kinetics of CO₂ Absorption into a Novel Reactive 4-diethylamino-2-butanol Solvent. *Chem. Eng. Sci.* 81, 251.
- [35] Pinsent, B. R. W.; Pearson, L.; Roughton, F. J. W., (1956). The Kinetics of Combination of CO₂ with OH⁻. *Trans. Faraday Soc.* 52, 1512.
- [36] Danckwerts, P. V.; Sharma, M. M., (1966). Absorption of Carbon Dioxide into Solutions of Alkalis and Amines (with Some Notes on Hydrogen Sulphide and Carbonyl Sulphide). *Institution of Chemical Engineers Review Series No.2 in the Chemical Engineer*. October, CE244-CE280.
- [37] Kohl, A. L.; Nielsen, R. B. *Gas Purification*, 5th ed; Gulf Publishing Company: Houston, 1997.
- [38] Lee, J. I.; Otto, F. D.; Mather, A. E., (1974). The Solubility of H₂S and CO₂ in Aqueous Monoethanolamine Solutions. *Can. J. Chem. Eng.* 52, 803-805.
- [39] Mathonat, C.; Majer, V.; Mather, A. E.; Grolier, J.-P. E., (1998). Use of Flow Calorimetry for Determining Enthalpies of Absorption and the Solubility of CO₂ in Aqueous Monoethanolamine Solutions. *Ind. Eng. Chem. Res.* 37, 4136-4141.
- [40] Carson, J. K.; Marsh, K. N.; Mather, A. E., (2000). Enthalpy of Solution of Carbon Dioxide in (Water + Monoethanolamine, or Diethanolamine, or N-Methyldiethanolamine) and (Water + Monoethanolamine + N-Methyldiethanolamine) at T = 298.15K. *J. Chem. Thermodyn.* 32, 1285-1296.
- [41] Kim, I.; Svendsen, H. F., (2007). Heat of Absorption of Carbon Dioxide (CO₂) in Monoethanolamine (MEA) and 2-(Aminoethyl)ethanolamine (AEEA) Solutions. *Ind. Eng. Chem. Res.* 46, 5803-5809.
- [42] Arcis, H.; Buserrolles, K. B.; Rodier, L.; Coxam, J.-Y., (2011) Enthalpy of Solution of Carbon Dioxide in Aqueous Solutions of Monoethanolamine at Temperature of 322.5K and 372.9K and Pressure up to 5 MPa. *J. Chem. Eng. Data.* 3351-3362.
- [43] Merkle, K. E.; Christensen, J. J.; Izatt, R. M., (1987). Enthalpies of Absorption of Carbon Dioxide in Aqueous Methyldiethanolamine Solutions. *Thermochim. Acta.* 121, 437-446.

-
- [44] Mathonat, C.; Majer, V.; Mather, A. E.; Grolier, J.-P. E., (1997). Enthalpies of Absorption and Solubility of CO₂ in Aqueous Solutions of Methyl-diethanolamine. *Fluid Phase Equilib.* 140, 171-182.
- [45] Pawlak, H. K. Enthalpies of Absorption and Solubility of CO₂ in Aqueous Solutions of Methyl-diethanolamine. *Sep. Sci. Technol.* 2007, 42, 2723-2737.
- [46] Kabadi, V. N. *Heat of Dissolution Measurement for CO₂ in Mixed Alkanolamine Solvents*. DOD Report, DE-FG26-03NT41912, 2005.
- [47] Arcis, H.; Rodier, L.; Buserrolles, K. B.; Coxam, J.-Y., (2008). Enthalpy of Solution of CO₂ in Aqueous Solutions of Methyl-diethanolamine at T = 322.5K and Pressure up to 5 MPa. *J. Chem. Thermodyn.* 40, 1022-1029.
- [48] Chowdhury, F. A.; Yamada, H.; Matsuzaki, Y.; Goto, K.; Higashii, T.; Onada, M., (2014). Development of Novel Synthetic Amine Absorbents for CO₂ Capture. *Energy Procedia.* 63, 572-579.
- [49] Arcis, A.; Rodier, L.; Coxam, J.-Y., (2007). Enthalpy of Solution of CO₂ in Aqueous Solutions of 2-Amino-2-methyl-1-propanol. *J. Chem. Thermodyn.* 39, 878-887.
- [50] Freeman, S. A.; Dugas, R.; vanWagener, D., (2010). Carbon Dioxide Capture with Concentrated Aqueous Piperazine. *Int. J. Greenh. Gas Control.* 4, 119-124.
- [51] Liu, J.; Wang, S.; Svendsen, H. F., (2012). Heat of Absorption of CO₂ in Aqueous Ammonia, Piperazine Solutions and Their Mixtures. *International Journal of Greenhouse Gas Control.* 9, 148-159.
- [52] Kim, Y. E.; Moon, S. J.; Yoon, Y. I.; Jeong, S. K.; Park, K. T.; Bae, S. T.; Nam, S. C., (2014). Heat of Absorption and Absorption Capacity of CO₂ in Aqueous Solutions of Amine Containing Multiple Amino Groups. *Sep. Purif. Technol.* 122, 112-118.
- [53] Kim, I.; Svendsen, H. F., (2011). Comparative Study of the Heats of Absorption of Post-Combustion CO₂ Adsorbents. *Int. J. Greenh. Gas Control.* 5, 390-395.
- [54] Pandya, J. D., (1983). Adiabatic Gas Absorption and Stripping with Chemical Reaction in Packed Towers. *Chem. Eng. Commun.* 19(4), 343-361.
- [55] Rocha, J. A.; Rocha, J. L.; Fair, J. R., (1993). Distillation-Columns Containing Structured Packings – a Comprehensive Model for Their Performance. 1. Hydraulic Models. *Ind. Eng. Chem. Res.* 32, 641-651.
- [56] Henriques de Brito, M. U. V. S.; Bangerer, A. M. B. P.; Laso, M., (1994). Effective Mass-Transfer Interfacial Area in a Pilot Column Equipped with Structured Packings and with Ceramic Rings. *Ind. Eng. Chem. Res.* 33, 647-656.
- [57] Brunazzi, E.; Nardini, G.; Paglianti, A.; Petarca, L., (1995). Interfacial Area of Mellapak Packing – Absorption of 1,1,1-Trichloroethane by Genosorb-300. *Chem. Eng. Technol.* 18, 248-255.
- [58] Rocha, J. A.; Rocha, J. L.; Fair, J. R., (1996). Distillation-Columns Containing Structured Packings – a Comprehensive Model for Their Performance. 2. Mass-Transfer Model. *Ind. Eng. Chem. Res.* 35, 1660-1667.
- [59] Gualito, J. J.; Cerino, F. J.; Cardenas, J. C.; Rocha, A. J., (1997). Design Method for Distillation Column Filled with Metallic, Ceramic or Plastic Structured Packing. *Ind. Eng. Chem. Res.* 36, 1747-1757.

- [60] Ataki, A.; Bart, H. J., (2006). Experimental and CFD Simulation Study for the Wetting of a Structured Packing Element with Liquids. *Chem. Eng. Technol.* 29, 336-347.
- [61] Sonderby, T. L.; Carlsen, K. B.; Fosbol, P. L.; Kiorboe, L. G.; von Solms, N., (2013). A New Pilot Absorber for CO₂ Capture from Flue Gases: Measuring and Modelling Capture with MEA Solution. *Int. J. Greenh. Gas Control.* 12, 181-192.