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Simulation of CO_2 capture by MEA scrubbing with a rate-based model

S. Moioli [a]*, L. A. Pellegrini, S. Gamba

Dipartimento di Chimica, Materiali e Ingegneria Chimica "G. Natta", Politecnico di Milano, Piazza Leonardo da Vinci 32, I-20133 Milano, Italy

Abstract

The most commonly used process for CO_2 capture is absorption by means of chemical solvents, such as alkanolamines. This consolidated technology can be applied to CO_2 removal from exhaust gas of power plants, natural gas and refinery gas. This paper focuses on CO_2 capture from exhaust gas by absorption with monoethanolamine (MEA). Thermodynamics, kinetics and mass transfer influence the chemical absorption process. Acidic gases and amines are weak electrolytes, which partially dissociate in the aqueous phase: the high non-ideality of the liquid phase must be properly taken into account when dealing with vapor-liquid equilibrium (VLE). Kinetics and mass transfer can be described using two different approaches: the "equilibrium-based stage efficiency" model or the "rate-based" one. The "equilibrium-based stage efficiency" approach corrects the performance of a theoretical stage by a factor called "stage efficiency". The "rate-based" model analyzes the mass and heat transfer phenomena that occur on a real tray or actual packing height. In ASPEN Plus®, that has been chosen as framework for the model proposed in this work, the prediction of mass transfer coefficients is based on the film theory by Lewis and Whitman, while other theories can more conveniently be used, i.e. the Eddy Diffusivity theory. Experimental data of a pilot plant for the purification of exhaust gas from power plant have been used to validate the model.The obtained results show an improvement in the representation of the absorption phenomenon.

Keywords: CO_2 capture; MEA scrubbing; absorption; rate-based model

[a]* Corresponding author. Tel.: +39 02 2399 3237; fax: +39 02 7063 8173.
E-mail address: stefania.moioli@mail.polimi.it

Nomenclature

a_{ij}	parameter for Electrolyte-NRTL theory
A	parameter for equilibrium constant expression
b_{ij}	parameter for Electrolyte-NRTL theory
B	parameter for equilibrium constant expression
C	parameter for equilibrium constant expression
D	parameter for equilibrium constant expression
D	diffusivity of carbon dioxide in the amine solution
E	eddy diffusivity
K_{H_2O}	equilibrium constant for the reaction of dissociation of water
K_{a,CO_2}	equilibrium constant for the reaction of dissociation of carbon dioxide
K_{a,HCO_3^-}	equilibrium constant for the reaction of dissociation of bicarbonate
$K_{a,MEAH^+}$	equilibrium constant for the reaction of protonation of monoethanolamine
K_{carb}	equilibrium constant for the reaction of dissociation of carbammate
$k_{c,MEA}$	kinetic constant for the reaction of carbon dioxide and monoethanolamine
k_{c,OH^-}	kinetic constant for the reaction of carbon dioxide and hydroxyl group
k_l°	mass transfer coefficient
τ_{ij}	parameter for Electrolyte-NRTL theory

1. Introduction

In many gas streams (such as natural gas, syngas, exhaust gases, and refinery gases) acid gases are often present. The presence of hydrogen sulfide and carbon dioxide is very undesirable due to corrosion, operational, economical and/or environmental reasons. CO_2 is a powerful greenhouse gas, whose massive presence in the atmosphere is the cause of gradual global warming. In order to limit this problem and to accomplish the requirements of the Kyoto protocol, its removal is realized by the treatment of combustion gases of power plants.

Industrially, carbon dioxide removal is mainly carried out using aqueous amine solvents because mass transfer is promoted by chemical reactions: acid gases can react directly or through a mechanism due to acid-base ionic species in solution. Moreover, molecules of alkanolamines are characterized by one hydroxyl group and one amino group. The former helps in reducing the vapor pressure and increasing water solubility, while the latter provides the necessary alkalinity in water solutions to make the acid gas

absorption occur [1]. Indeed, the solubility of acid gas in water is highly influenced by the presence of the amine.

The mass transfer from the bulk of the gas phase to the bulk of the liquid phase can be described through the following steps:

1. diffusion of the component from the bulk of the gas phase to the gas-liquid interface;
2. diffusion of reagents from the gas-liquid interface to the bulk of the liquid phase;
3. simultaneous reaction between dissolved gas and liquid reactant;
4. diffusion of reaction products in the bulk of the liquid phase promoted by the concentration gradient due to chemical reaction.
5.

Acid gases reach physical equilibrium in the vapor phase with the same molecular unreacted acid gases in water. The equilibrium solubility of an acid gas that does not react in an aqueous solution containing a reactive solvent is then governed by the partial pressure of this gas over the liquid. In a reactive solvent, on the contrary, when an acid gas is absorbed, it is partially consumed by chemical reactions. As a consequence, the CO_2 bulk concentration in the liquid phase is low and the rate of absorption of the acid gas is significantly affected by the amine. Chemical reactions enhance the driving force for mass transfer, that is the difference between the gas concentration in the liquid at the gas-liquid interface and the unreacted gas concentration in the bulk of the liquid phase.

This work focuses on CO_2 capture from exhaust gases of power plants by absorption with an aqueous solutions of monoethanolamine (MEA). This amine is the most frequently used solvent for this process, due to its relatively high loading, i.e. the ratio of moles of absorbed acid gas per mole of amine.

The modeling procedure has to take into account both thermodynamics and mass transfer [2]. Kinetics and mass transfer can be described using two different approaches: the "equilibrium-based stage efficiency" model or the "rate-based" one [3,4]. The "equilibrium-based stage efficiency" approach corrects the performance of a theoretical stage by a factor called "stage efficiency". It takes into account mass transfer and non equilibrium chemical reactions for all species (ASPEN HYSYS[®] [5]) or only mass transfer for non reactive species, when kinetics is considered (ProMax[®] [6]).

The "rate-based" model avoids the approximation of efficiency, by analyzing the mass and heat transfer phenomena that occur on a real tray or actual packing height [7]. In ASPEN Plus[®] [8] the prediction of mass transfer coefficients is based on the film theory by Lewis and Whitman [9], while other theories can more conveniently be used, i.e. the Eddy Diffusivity theory [10].

ASPEN Plus[®] simulator was found suitable for user customization and it has been chosen as framework for the model proposed in this work.

The experimental data of a pilot plant for the purification of exhaust gas from a power plant [11] have been used to check the performances of the simulator.

The obtained results show an improvement in the representation of the absorption phenomenon.
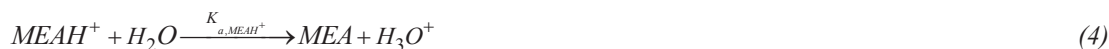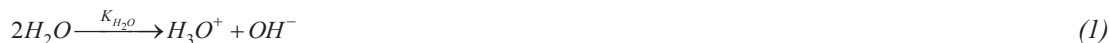
2. Modeling

2.1. Thermodynamics and chemical equilibria

A good description of vapor-liquid equilibrium is crucial for a correct design of unit operations involving mass transfer from one phase to the other [12-16].

Chemical reactions in the liquid phase should be taken into account when describing the VLE, also because the system is strongly non-ideal due to the generation of ionic species. Acid gases and amines are weak electrolytes and they partially dissociate in the aqueous phase. The liquid phase is then composed of

a moderately volatile solvent (water), a non volatile solvent (MEA), very volatile molecular species (acid gas) and non volatile ionic species [2].

Physical VLE involves only molecular species, i.e., CO_2, H_2O and MEA. Chemical reactions occurring in the liquid phase involve both molecular and ionic species and can be described according to the equilibrium expressions (Eqs. (1)-(5)).

$$2H_2O \xrightarrow{K_{H_2O}} H_3O^+ + OH^- \tag{1}$$

$$2H_2O + CO_2 \xrightarrow{K_{a,CO_2}} HCO_3^- + H_3O^+ \tag{2}$$

$$H_2O + HCO_3^- \xrightarrow{K_{a,HCO_3^-}} CO_3^{2-} + H_3O^+ \tag{3}$$

$$MEAH^+ + H_2O \xrightarrow{K_{a,MEAH^+}} MEA + H_3O^+ \tag{4}$$

$$MEACOO^- + H_2O \xrightarrow{K_{carb}} MEA + HCO_3^- \tag{5}$$

The equilibrium constants K_j are strongly dependent on temperature T, as described in Eq. (6):

$$\ln K_j = A_j + \frac{B_j}{T} + C_j \ln T + D_j T \tag{6}$$

where A_j, B_j, C_j, D_j are parameters whose values can be found in literature [8,17,18]. Values used for the simulation are reported in Table 1. Both literature sources (for dissociation constants of water, carbon dioxide and bicarbonate) and ASPEN Plus® default values (for dissociation constants of protonated monoethanolamine and carbammate) are taken into account.

Table 1. Parameters A, B, C and D for the equilibrium constants of Eqs. (1)-(5).

Reaction	A	B	C	D	Source
Eq. (1)	132.89	-13446	-22.47	0	[17]
Eq. (2)	231.46	-12092	-36.78	0	[18]
Eq. (3)	216.05	-12432	-35.48	0	[17]
Eq. (4)	-3.038	-7008.3	0	-0.0031	[8]
Eq. (5)	-0.52	-2545.5	0	0	[8]

To describe vapor-liquid equilibrium, a γ/Φ approach is used. The vapor phase is represented by means of an Equation of State (EoS), the SRK EoS [19]. The liquid phase is described by means of an activity coefficient model. For this system, the Electrolyte-NRTL model [20-23] is used, and it takes into account the excess Gibbs free energy. This thermodynamic function can be obtained as the sum of two contributions, one due to short range or local interactions (NRTL [24]) that exist in the immediate vicinity of a component and one due to long range (LR) ion-ion interactions.

It is based on the like-ion repulsion assumption and on the local electroneutrality assumption. The former states that the local composition of cations around other cations is zero and, similarly, the local composition of anions around other anions is zero. This idea is based on the assumption that repulsive

forces between ions of the same charge are strong, therefore they are extremely relevant for near species. The local electroneutrality assumption, on the other hand, implies that the distribution of anions and cations around a central molecule makes the net local charge null.

The model can be used to reproduce experimental data for a wider range of temperatures and loadings. It is characterized by a large number of parameters, that take into account interactions between molecule and molecule, molecule and ion pair, ion pair and ion pair. Binary parameters vary with temperature according to Eq. (7).

$$\tau_{ij} = a_{ij} + \frac{b_{ij}}{T} \tag{7}$$

Vapor-liquid equilibrium experimental data for the system CO_2-H_2O-MEA have been collected over the past two decades. In order to obtain a reliable model, calibrated parameters were obtained by regression, as widely described in a previous work [2].

2.2. Mass transfer with chemical reaction: kinetics

The process of absorption of carbon dioxide in the amine solution involves finite-rate reactions. Due to chemical reactions, a further contribution to mass transfer should be taken into account. Besides diffusion limitations, also kinetics of reactions between CO_2 and MEA (Eq. (8)) and between CO_2 and OH^- (Eq. (9)) must be considered. Even though these reactions are quite fast at the conditions of the system, chemical equilibrium is not attained.

$$CO_2 + MEA + H_2O \xrightarrow{k_{c,MEA}} MEACOO^- + H_3O^+ \tag{8}$$

$$CO_2 + OH^- \xrightarrow{k_{c,OH^-}} HCO_3^- \tag{9}$$

For these two reactions, rate equations can be written as Eq. (10) and Eq. (11).

$$R_{CO_2+MEA} = k_{c,MEA}[CO_2][MEA] \tag{10}$$

$$R_{CO_2+OH^-} = k_{c,OH^-}[CO_2][OH^-] \tag{11}$$

Rate constants are expressed according to the Arrhenius relationship. Values of the pre-exponential factor and of the activation energy are taken from literature [25,26] and are reported in Table 2.

Table 2. Values of kinetic constants of Eq. (8) and Eq. (9).

Reaction	A [m^3/(kmol s)]	Eact [kJ/mol]	Source
8	4.32×10^{13}	55.4603	[25]
9	9.77×10^{10}	41.2564	[26]

2.3. Mass transfer: film theory

The film theory was proposed by Lewis and Whitman in 1924 [9] and it is the first approach to mass transfer analysis at vapor-liquid interface. This theory assumes steady state conditions and it is implemented in ASPEN Plus® by default.

It is based on the hypothesis that all the mass transfer resistances are located in two films of a finite thickness. These films are near the interface on the gas side and on the liquid side.

When contact between liquid and gas phase occurs, on the gas phase of the interface there exists a layer in which motion by convection is slight compared to that in the bulk of the gas phase. A similar behavior is seen on the liquid side of the interface, where there is a layer of liquid which is free from mixing by convection. By assuming that these films are free from convection currents, any transfer of solute through these films is affected by the process of diffusion. Therefore, they represent the controlling resistances to mass transfer from one phase to another. In the bulk of the liquid or of the gas phase, on the contrary, mixing by convection is so rapid that the concentration of solute in the phase can be considered uniform everywhere.

When absorption occurs without chemical reaction, film theory predicts a straight line concentration gradient both in the gas and in the liquid film, for species which transfer between phases.

The rate of diffusion through the gas film is proportional to the difference between solute concentrations at the bulk and at the interface. Diffusion through the liquid film, on the contrary, is controlled by the difference between the concentration of solute in the liquid at the interface and its concentration in the bulk of the liquid.

Being the surface films very thin, the actual amount of solute there contained can be considered at any time negligible compared to the amount diffusing through them. Indeed, all the solute that passes through one film must also pass through the other: the two films are two diffusional resistances in series. Sometimes one of the two films exerts a greater influence than the other one, that can be negligible. If so, the system can be considered as composed of only one film.

The driving force that allows diffusion depends on the concentration difference through either of the two films.

A mass transfer coefficient can be derived, and it is proportional to diffusivity of carbon dioxide in the aqueous phase, according to Eq. (12).

$$k_l^\circ = \frac{D_{CO_2}}{\delta} \tag{12}$$

This dependence, however, does not match what experimentally observed, that is characterized by a square root dependence on diffusivity coefficient, as can be obtained using the Eddy diffusivity theory [10].

2.4. Eddy diffusivity theory

The Eddy diffusivity theory [10] assumes steady state conditions and takes into account both molecular diffusion and turbulent transport. This theory takes into account the presence of little eddies that influence the mass transfer rate.

All species change their concentration from the value at the interface to the value in the liquid bulk in a primary mass transfer resistance zone. The curvature radius of the interface should be taken into account: the free liquid surface can be considered planar, even if it is not, if the length of the local curvature radius

is higher than the primary resistance zone depth. Since this zone is usually thin compared to the liquid phase, a semi-infinite coordinate perpendicular to the interface surface can be considered.

The expression for eddy diffusivity is reported in Eq. (13).

$$E = \varepsilon x^n + b \tag{13}$$

where x is the distance from the interface along the semi-infinite coordinate and $n = 2$. At the interface there is no influence of eddies, so $b = 0$. Far from the interface, on the contrary, eddy diffusivity becomes the most important phenomenon.

A mass transfer coefficient can be obtained (Eq. (14)), where a square root dependence on diffusivity is shown.

$$k_l^\circ = \frac{2}{\pi} \sqrt{D_{CO_2} \varepsilon} \tag{14}$$

This theory is then able to predict the correct dependence on diffusivity without complicating the model by introducing a dependence on time, as other theories [27,28] do, and was used for simulation.

3. Validation of simulation results with experimental data from a pilot plant

3.1. Pilot plant description

The model was tested by simulating an experimental pilot plant [11] shown in Fig. 1, where carbon dioxide is removed with an aqueous solution of monoethanolamine 30% w/w.

The absorption column consists of two 3.05 m beds of packing, with a collector plate and a distributor between the two beds. The main characteristics of the column are reported in Table 3. For a detailed description refer to [11].

Table 3. Characteristics of the experimental absorption column [11].

Parameter	Value	Parameter	Value
Diameter [m]	0.427	Packing type	*IMPT #40*
Total packing height [m]	6.10	Pressure [bar]	1.01

The gas fed to the absorption column is characterized by a composition similar to the one of exhaust gases coming out of coal-fired power plants. Many cases, which experimental data are available for, were simulated. In Table 4 the molar composition of the streams entering the absorber of one of the simulated cases are shown.
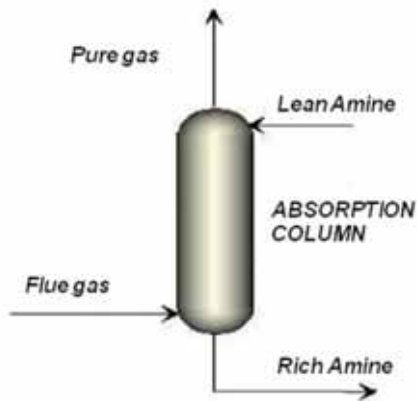
Fig. 1. Schematic of the experimental [11] and simulated absorption column.

Table 4. Molar composition of the streams entering the absorption column [11].

Component	Exhaust gas	MEA solvent
H_2O	0.0160	0.8512
MEA	0	0.1209
CO_2	0.1841	0.0279
N_2	0.7528	0
O_2	0.0471	0

3.2. Results

Results are shown in Fig. 2 and in Fig. 3. In Fig. 3 two values of experimental data are shown at a height of 3.1 m from the bottom. This is due to the fact that in the pilot column a flow distributor is inserted between the two packing beds: this tool helps in improving the column efficiency, but causes heat dissipations. The two temperature values are obtained measuring the temperature above and below the distributor and for sake of completeness both of them are reported. ASPEN Plus® well describes the temperature profile along the column, but predicts a CO_2 removal higher than the experimental one. Another model [29] does not provide a good temperature profile nor a good prediction of carbon dioxide concentration in the pure gas.

With our model the absorption tends to be slower, so that the concentration of carbon dioxide is close to experimental data. The use of Eddy diffusivity theory helps in describing accurately both the amount of CO_2 removed and the temperature profile.
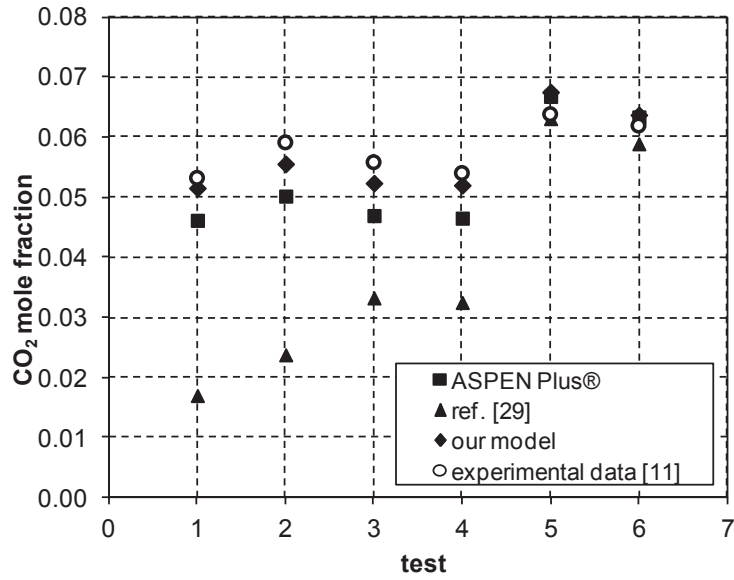
Fig. 2. Carbon dioxide molar fraction in the pure gas coming out of the absorber.
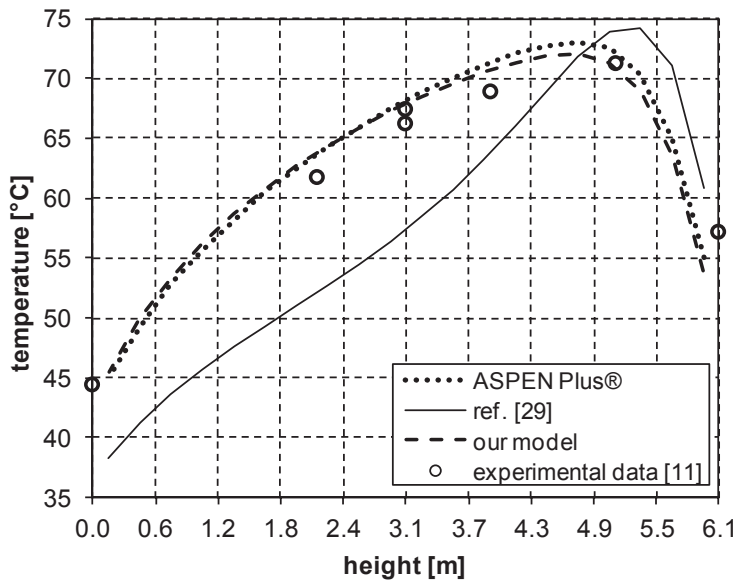

Fig. 3. Temperature profile for the case reported in Table 4.

4. Conclusions

Mass transfer significantly influences the process of absorption of acid gases in amine aqueous solutions. In this work a new model is presented, where the Eddy diffusivity theory is taken into account.

The model has been verified by comparing simulation results with experimental data of a pilot plant [10]. An improvement in the prediction of experimental data and a better representation of the absorption phenomenon have been obtained.

This work can be usefully applied to design of acid gas absorption plants with amines. The possibility of using a reliable model, tested on experimental data, allows engineering companies to design more accurate plants and to choose the right amount of amine solvent to be used.

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