The rate-based modelling of CO_2 removal from the flue gases of power plants

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Abstract

Recently, global warming has become a topic of great interest, involving social, economic and industrial issues. Many efforts are being made in order to limit emissions of CO_2, a powerful greenhouse gas, whose massive presence in the atmosphere is increasing more and more. Industrially the most commonly used process for CO_2 capture is absorption by alkanolamines, widely applied to the removal of exhaust gases from power plants. The design of the absorber is still difficult, due to the different phenomena involved. Commercially, several process simulators can be found, based on different assumptions, both for thermodynamics and for diffusion with reaction. Thermodynamics, kinetics and mass transfer greatly influence the chemical absorption process. Acid 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, usually with a γ/ϕ method. Kinetics and mass transfer can be described using two different approaches: the "equilibrium-based stage efficiency" or the "rate-based" one. This latter, if based on a proper mass transfer theory, can be used to correctly describe the phenomenon of diffusion with reaction occurring from the vapor phase to the liquid phase.

This paper focuses on modelling the absorption of CO_2 by means of a piperazine solution, performed by properly modifying ASPEN Plus® with a homemade subroutine linked to the simulator. Experimental data of a pilot plant for cleaning flue gases from power plants has been used to validate the model, which represents the absorption phenomenon well.

Keywords: CO_2 removal, amine scrubbing, rate-based modelling, piperazine, thermodynamics, flue gases, power plants, greenhouse gas.

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1 Introduction

Recently global warming has become a topic of great interest, involving social, economic and industrial issues [1]. Energy markets and their sustainability are nowadays the focus of both public and private interest [2]. Many efforts are being made in order to limit emissions of CO_2, a powerful greenhouse gas (GHG), whose massive presence in the atmosphere is increasing more and more: climate scientists have observed that the 2012 concentration of CO_2 was about 40% higher than the mid-1800s one, with an average of growth of 2 ppmv/year in the last ten years [1]. The problem is that even after stabilization of the atmospheric GHG concentration, anthropogenic warming would continue for centuries due to the time scales associated with climate processes and feedbacks. According to the International Energy Agency [1], stabilizing concentrations would require a large reductions of global CO_2 emissions from current levels.

The use of energy is the largest source of anthropogenic emissions of greenhouse gases, the oxidation of carbon in fuels during combustion being the major CO_2 production process within the energy sector. As compared to gas, coal is nearly twice as emission intensive on average (being carbon emission factors 15.3 tC/TJ for gas, 16.8–27.5 tC/TJ for oil product and 25.8–29.1 tC/TJ for primary coal products). Though representing only the 29% of the world energy consumption in 2011, its heavy carbon content per unit of energy released makes coal accounting for about 44% of the global CO_2 emissions.

Industrially in order to limit CO_2 emissions, the most commonly used process is absorption by alkanolamines, widely applied to the removal of exhaust gases from coal fired power plants.

The design of the absorber is still difficult, due to the different phenomena involved. Commercially, several process simulators can be found, based on different assumptions, both for thermodynamics and for diffusion with reaction, but they are not always as reliable as needed.

This paper focuses on modelling the absorption of CO_2 by means of a piperazine solution, performed by properly modifying ASPEN Plus® with a homemade kinetic/mass transfer subroutine linked to the simulator.

Experimental data of a pilot plant for cleaning flue gases from power plants by means of piperazine scrubbing have been used to validate the model, which well represents the absorption phenomenon.

2 The pilot plant

Experimental data [3] of a pilot plant for the CO_2 removal section of flue gases coming from a coal fired power plant are available and have been used to test the commercial simulator ASPEN Plus® and to validate the modified method used in this work.

An absorption column, operating at atmospheric pressure and composed of two sections of structured packing of total height equal to 6.1 m, is fed with a gaseous stream containing CO_2, N_2, O_2 and H_2O with the aim of removing carbon dioxide with an aqueous solution of PZ as amine solvent. This solvent has recently started to be considered advantageous because of the improved capacity and rate of reaction, if compared to other amine solutions, and can be successfully used to purify flue gases from power plants. For a better description of the experimental system, please refer to Plaza [3].

All the 14 test runs of the "*Nov'08*" campaign have been taken into account, though for sake of conciseness only the most relevant are shown.

3 Modelling of amine scrubbing systems

An accurate description of the phenomenon involved in amine scrubbing systems, in terms of thermodynamics [4–6], kinetics and mass transfer [7–9], is fundamental for a reliable representation of the absorption process.

3.1 Thermodynamic modelling

Acid gases and amines are weak electrolytes and they partially dissociate in the liquid phase, whose main component is water. In the liquid phase, then, water and amine are in mixture with very volatile molecular species (carbon dioxide) and non-volatile ionic species, not present in the vapour phase. Generally, when dealing with process simulations, a proper thermodynamic model is fundamental to model vapour-liquid equilibrium [10, 11].

To describe the vapour-liquid equilibrium of this non-ideal system, a γ/ϕ approach has been used. The Electrolyte-NRTL model (already implemented in ASPEN Plus®), developed by Chen and co-workers [12–15] and tested against experimental data [16, 17] in a previous work [18], has been used for the representation of the thermodynamic behaviour of the system.

3.2 Diffusion with reaction modelling

Kinetics and mass transfer can be described by means of the "equilibrium based stage efficiency" approach or of the "rate based" one [19]. The former corrects the performance of a theoretical stage by using a stage efficiency, while the latter takes into account the real mass and heat transfer phenomena that occur on a real tray or on an actual packing height. With nonreactive systems, the tray efficiency can be determined by considering gas and liquid properties, tray design and fluid dynamics; with reactive systems, the correlation for tray efficiency is more complex because the reactions affect both the vapour-liquid equilibrium relationship and the rate of absorption and efficiency cannot be kept constant along the column. However, the "equilibrium-based stage" approach is widely used also in amine scrubbing modelling, because it is not demanding in terms of computational time. On the contrary, the "rate-based stage" approach is more CPU consuming and convergence is not always easily achievable, because of the large number of simultaneous equations to be solved. However, being developed on a theoretical basis, the "rate-based stage" approach is considered the most reliable method for amine scrubbing modelling [20].

ASPEN Plus® process simulator is provided with both the "equilibrium stage efficiency" and with the "rate-based" models. Far from other software, such as

ASPEN HYSYS® [21], provided with methods to calculate proper efficiencies for each gaseous species involved in the absorption phenomenon, efficiency for the equilibrium approach in ASPEN Plus® has to be given by the user. The "rate-based" model is by default based on the Film theory, developed by Lewis and Withman [22] in 1924.

According to Film theory, all the mass transfer resistances are located into two films of a finite thickness close to the interface on the gas side and on the liquid side. These two films represent the controlling resistances to mass transfer from one phase to the other, since, in the bulk of the liquid or of the gas phases, mixing by convection is so fast that the concentration of solute can be considered uniform.

A mass transfer coefficient can be derived, and it is proportional to the diffusivity of carbon dioxide in the solvent, according to:

$$k_l^{\circ} = \frac{D_{CO_2}}{\delta} \tag{1}$$

The results of the simulations of the experimental data [3] taken from a pilot plant for removal of CO_2 from flue gases of a coal fired power plant performed with the ASPEN Plus® default model are reported in 1 and 2.

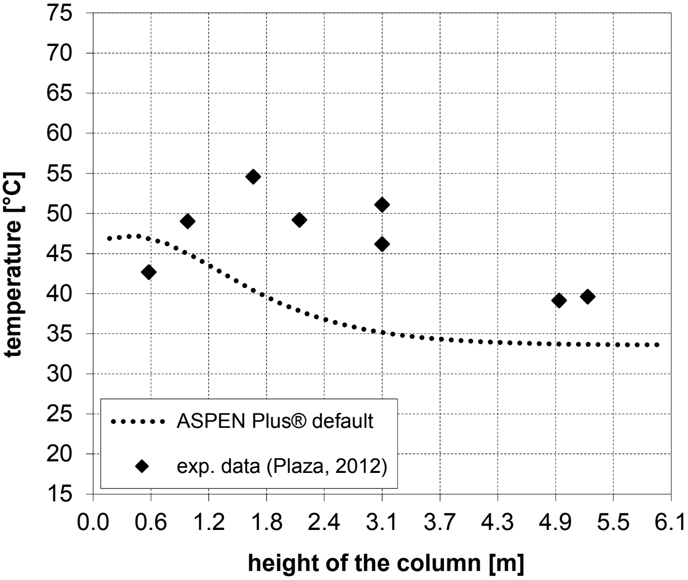

Figure 1: Results of simulation of experimental test #7 performed with ASPEN Plus® default model.

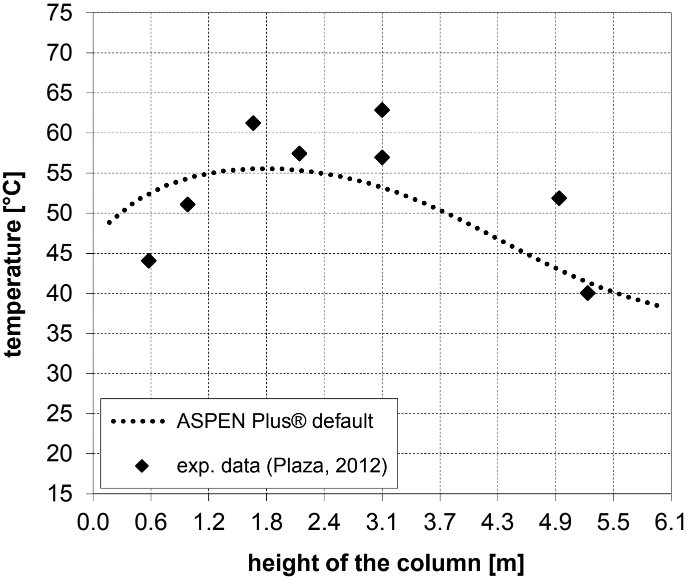

Figure 2: Results of simulation of experimental test #8 performed with ASPEN Plus® default model.

The temperature profile along the column is of great importance when dealing with simulations of these kinds of systems, since the amount of heat released during the process is proportional to the amount of absorbed carbon dioxide. The temperature profile described by ASPEN Plus® is not so close to the experimental trend, in particular as of the position of the bulge.

4 Reactions occurring in the liquid phase

Amine scrubbing involves the presence of chemical reactions occurring in the liquid phase. The thermodynamic description should take into account chemical equilibrium reactions, while the phenomenon of diffusion with reaction should be modelled considering also kinetic-controlled reactions.

The set of chemical equilibrium reactions is composed of eqns (2)–(8), whose chemical equilibrium constant is calculated according to eqn (9).

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

$$CO_2 + 2H_2O \xrightleftharpoons{K_{a,CO_2}} HCO_3^- + H_3O^+ \tag{3}$$

$$H_2O + HCO_3^- \xrightleftharpoons{K_{a,HCO_3^-}} CO_3^{2-} + H_3O^+ \tag{4}$$

$$PZH^+ + H_2O \xrightleftharpoons{K_{a,PZH^+}} PZ + H_3O^+ \tag{5}$$

$$PZ + HCO_3^- \xrightleftharpoons{K_{PZCOO^-}} PZCOO^- + H_2O \tag{6}$$

$$HPZCOO + H_2O \xrightleftharpoons{K_{HPZCOO}} PZCOO^- + H_3O^+ \tag{7}$$

$$PZCOO^- + HCO_3^- \xrightleftharpoons{K_{PZ(COO^-)_2}} PZ(COO^-)_2 + H_2O \tag{8}$$

$$\ln K_j = A_j + \frac{B_j}{T} + C_j \ln T + D_j T \tag{9}$$

The sources of values for parameters used in each reaction are reported in .

Table 1: Sources of values of parameters for chemical equilibrium constant of reactions eqns (2)–(8) used in this work.

Reaction	**Source**
dissociation of water (eqn (2))	Edwards *et al.* [23]
dissociation of carbon dioxide (eqn (3))	Edwards *et al.* [23]
dissociation of the bicarbonate ion (eqn (4))	Edwards *et al.* [23]
reaction of protonated PZ (eqn (5))	Moioli and Pellegrini [18]
formation of the piperazine carbamate from piperazine and bicarbonate (eqn (6))	Bishnoi and Rochelle [24]
dissociation of HPZCOO (eqn (7))	ASPEN Plus®
formation of the piperazine dicarbamate (eqn (8))	ASPEN Plus®

For a correct representation of the mass transfer of carbon dioxide from the vapour phase to the liquid phase, kinetics of reactions should be considered, in particular for reactions involving CO_2: though being quite fast at the operating conditions of the system, they do not attain equilibrium.

In addition to the chemical equilibrium reactions not involving carbon dioxide, the following kinetic-controlled mechanism, then, has been taken into account.

$$PZ + CO_2 + H_2O \xrightarrow{k_{f,PZ}} PZCOO^- + H_3O^+ \tag{10}$$

$$PZCOO^- + H_3O^+ \xrightarrow{k_{b,PZ}} PZ + CO_2 + H_2O \tag{11}$$

$$PZCOO^- + CO_2 + H_2O \xrightarrow{k_{f,PZCOO^-}} PZ\left(COO^-\right)_2 + H_3O^+ \tag{12}$$

$$PZ\left(COO^-\right)_2 + H_3O^+ \xrightarrow{k_{b,PZCOO^-}} PZCOO^- + CO_2 + H_2O \tag{13}$$

$$CO_2 + OH^- \xrightarrow{k_{f,OH^-}} HCO_3^- \tag{14}$$

$$HCO_3^- \xrightarrow{k_{b,OH^-}} CO_2 + OH^- \tag{15}$$

$$k_j = A_j \exp\left(-\frac{E_{att,j}}{RT}\right) \tag{16}$$

A comparison among the existing correlations found in literature would have been of great interest if experimental data had been available. In the absence, the kinetic constant of the reaction of carbon dioxide and piperazine in water has been calculated according to ASPEN Plus® [25], while the one of the reaction of carbon dioxide and the carbammate ion has been taken as ¼ of the kinetic constant of the reaction involving PZ and CO_2, as done by Dang and Rochelle [26]. This reaction, however, does not exert a strong influence on the behaviour of the absorption column [18], but it has been considered for a complete description of the process. The kinetic constant of reactions eqn (14) has been calculated according to Pinsent *et al.* [27].

The kinetic constants of the backward reactions have been computed by considering the one of the forward reaction and the chemical equilibrium constant of the corresponding reaction.

5 The used mass-transfer model

A deep insight into the mass transfer phenomenon has shown an inaccuracy of the film theory, used by default in ASPEN Plus®, when applied to simulations of amine scrubbing processes. Indeed, as stated also by Astarita *et al.* [28]:

> *"Empirical mass transfer coefficient correlations available in the literature for a liquid in contact with a gas consistently indicate that, in fact,* k_L° *is proportional to the square root of* D *".*

Many theories consider a non-linear dependence on diffusivity of carbon dioxide in the solvent for mass transfer coefficient, such as the theory by Higbie [29], the one by Danckwerts [30] and the Eddy Diffusivity theory [31]. This latter is a steady-state theory and has been used in this work.

It takes into account both molecular diffusion and turbulent transport, by considering 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:

$$E = \varepsilon x^n + b \tag{17}$$

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, where a square root dependence on diffusivity is shown:

$$k_l^{\circ} = \frac{2}{\pi}\sqrt{D_{CO_2}\varepsilon} \tag{18}$$

This theory is able to predict the correct dependence on diffusivity without complicating the model by introducing a dependence on time, as other theories do, and was used in this work.

Considering the contribute of eddy diffusivity to mass transfer and the presence of chemical reactions, the mass balance equation for carbon dioxide is:

$$\frac{\partial}{\partial x}\left[\left(D_{CO_2} + \varepsilon x^2\right)\frac{\partial[CO_2]}{\partial x}\right] - R_{CO_2} = 0 \tag{19}$$

where R_{CO_2} is the rate of consumption of carbon dioxide due to chemical reactions occurring in the liquid phase, D_{CO_2} the molecular diffusivity and ε the parameter for Eddy Diffusivity of carbon dioxide in the solvent.

Because these reactions can be considered fast, with good approximation the Interface Pseudo First Order (IPFO) assumption can be taken into account [7, 8, 18]. According to this, reactions occur only in a small region close to the interface, the reaction sub-layer, which is a part of the boundary layer, and the concentrations of all species except CO_2 are assumed not to significantly change from their value at the interface. The extent of the reaction sub-layer depends on the kinetics involved [18]. In the boundary layer region, not interested by kinetic-controlled reactions, diffusion occurs, causing the liquid bulk concentration being different from that resulting in the reaction sublayer.

A homemade subroutine has been linked to the simulator to test the proposed model on the basis of experimental data of removal of carbon dioxide from flue gases of power plants.

6 Results and discussion

Simulation results and experimental data of some test runs are shown in Figures 3 and 4.

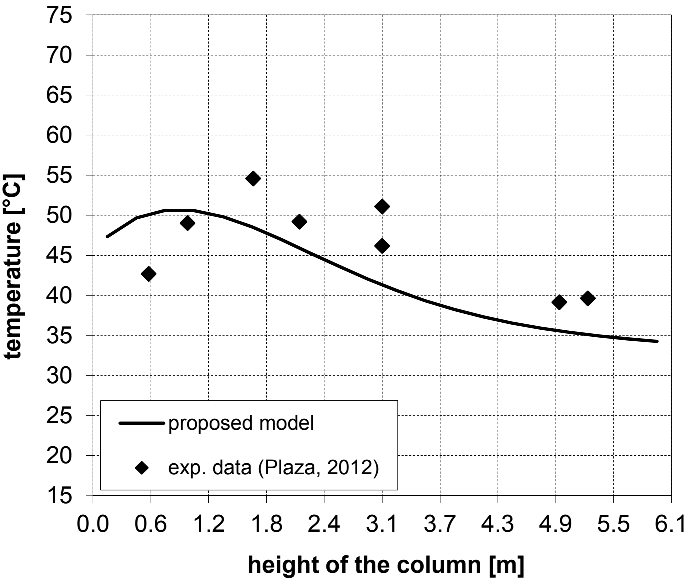

Figure 3: Results of simulation of experimental test #7 performed with the proposed model.

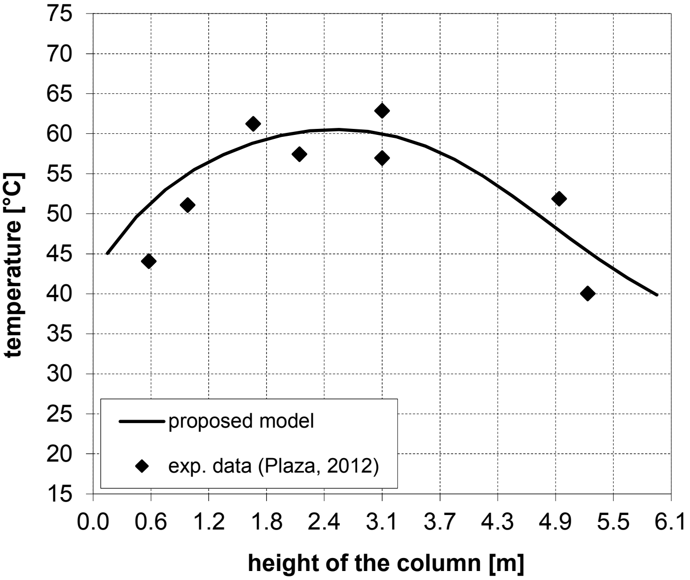

Figure 4: Results of simulation of experimental test #8 performed with the proposed model.

No experimental values of carbon dioxide molar fraction are available; however, for amine scrubbing systems the temperature profile can be considered an index of the reliability of the model, because heat is released during the absorption of CO_2. The exothermic reactions occurring in the liquid phase causes the formation of a bulge, whose extent and position strongly depend on the amount of absorbed acid gas and on the ratio between the liquid and the vapour flows [19].

The model based on the Eddy Diffusivity theory shows more accuracy than the one based on film theory (ASPEN Plus® default), without using any adjustable parameter, so it can also well represent the amount of removed CO_2 [7].

7 Conclusion

Mass transfer significantly influences the process of absorption of acid gases in amine aqueous solutions. In this work a model different from ASPEN Plus® default 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 [3]. 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 improve their accuracy in designing and running PZ scrubbing plants.

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