

MODELLING OF CO₂ ABSORPTION IN GAS TREATMENT UNITS

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Abstract

The combustion of fossil fuel produces large amounts of carbon dioxide (CO₂) gas that must be removed due to its environmental impacts. The absorption of CO₂ in alkanolamine solution of mono-ethanolamine (MEA) is considered the most effective separation process. In this paper, a model of CO₂ separation from a gas stream by a solution of MEA in a packed tower has been mathematically developed for unsteady state predictions. The rate-base model has been adopted as it considers the entire phenomenon occurring during the absorption process. The methodology of the dynamic modelling of the isothermal CO₂ chemical absorption was created. The results were obtained in terms of the CO₂ partial pressure and the MEA concentration gradients against the column height and time. In addition, the effect of the MEA concentration to the CO₂ partial pressure ratio and the liquid to gas flow rate ratio on the column performance has been investigated. The developed model has been validated for the steady state operation of experimental data where satisfied agreement has been noticed.

Keywords: Absorption; Packed Column;; Dynamic Modelling; steady state operation

Introduction

Carbon dioxide is considered as one of the most effective greenhouse gases because its concentration increase in the air is believed to be the reason for the global warming phenomena. Power plants are responsible for releasing the largest portion of CO₂ into the atmosphere nowadays. As coal-fired plants are utilised to generate nearly 40% of the total world's electricity, the rate of CO₂ emissions due to coal burning is considered the highest compared to the petroleum and the natural gas (Henderson, 2003). Since the world has become aware of the need to limit the greenhouse gases release, the industrialised countries that produce the largest percentage of such gases have obligated to reduce emissions to targeted levels (UNFCCC, 2010). The reduction in CO₂ emissions levels requires a decrease in the energy demand, an increase in the power plants efficiencies and an efficient system for the CO₂ capture from the flue gas streams.

The absorption process is intensively applied in petroleum, natural gas and chemical industries (Meisen and Shuai, 2018). The process principle relies on a chemical reaction between the gaseous pollutant (CO_2) and an aqueous liquid solution containing a reactive solvent. The typical unit of CO_2 absorption by the MEA solution is shown in Figure 1. The flue gas stream generated from coal-fired power plants contains approximately 10-15% of CO_2 (Lawala et al ,2009). The flue gases fed from the bottom of the absorption column at a relatively low temperature ranging from 30 to 40°C. A direct contact with the mono-ethanolamine (MEA) aqueous solution is made counter-currently over a packing material for providing a great contact area. Mass transfer between phases followed by a chemical reaction takes place along the column length. The CO_2 -rich amine solution leaves from the bottom and then it is pumped to the desorber after being heated by coming CO_2 -lean amine solution through a heat exchanger. The CO_2 -rich solution is treated thermally in the desorber to release CO_2 , which is then collected at the topping condenser from which condensed water is refluxed to the column. The CO_2 free lean amine is recycled to the absorber for new absorption batch.

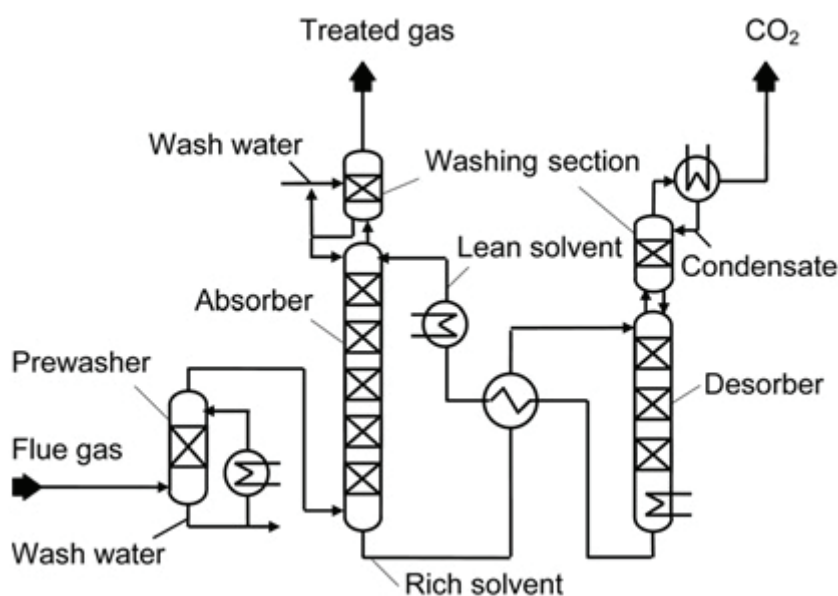


Figure 1. Flow sheet of the amine absorption unit (Mangalapally and Hasse, 2011).

Many studies have been revealed considering the steady state operation of the process, aiming to achieve the best process performance by which a high removal rate of the pollutant is obtained (Pintola, Tontiwachukwuthikul and Meisen, 1993), (Al-Baghli et al, 2001). However, the unsteady state operation at transient conditions of CO_2 loading variation and start-up operation has not been extensively studied (Eterigo and Olutoye, 2008), (Kumazawa, Sohn and Park, 2002). The dynamic or

unsteady state modelling is necessary for prediction of the effect of transient condition on the absorption process. This type of simulator investigates the process performance under exceptional conditions and shows the effect of such state on the integration between the parts of the process, absorber and desorber (Kvamsdala, Jakobsena and Hoff, 2009). The variation of CO₂ loading is considered the most common case of transient conditions occurring due to disturbance in downstream power plant. This case can be addressed through considering the dynamic trend of the plant. The dynamic model is benefited to determine the manner in which the optimal operating conditions should be maintained.

The main objective of this research is the development of a mathematical model for the post-combustion CO₂ absorption process in a packed tower using MEA aqueous solution. The model is developed to be used in the case of unsteady state CO₂ absorption process. The application of the model for simulating real cases of dynamic operation will be finally made.

Absorption Model Development

The CO₂ absorption model was developed in terms of most important parameters that effect the absorption process. Partial pressure of CO₂ is considered as a dependent parameter which depend on a gas absorption column height (z) and unsteady state time interval (t). In order to simulate the unsteady state conditions, the present model follows the following assumptions:

1. Counter current flow with well mixed between vapour and liquid.
2. Plug flow regime.
3. The evaporation of solvent is negligible.
4. The heat to surrounding is very small so isothermal conditions is assumed.
5. The chemical reaction is very fast and take place in liquid phase.

Gas-Phase Mass Balance

The general continuity equation of mass transfer for gas phase associated with a chemical reaction is used to determine the CO₂ concentration, C_{CO2}, as a function of length and time. The continuity equation used for unsteady state mass transfer within cylindrical coordinates, z, and time, t

$$\frac{\partial C_{CO2}}{\partial t} + u_z \frac{\partial C_{CO2}}{\partial z} = S_{CO2} \quad (1)$$

Where u_z , S_{CO2} , are the gas superficial velocity and the source term respectively. The mathematical simulation is carried out by using MATLAB package that is employed to solve the discretised system of partial differential equations. The discretisation of Equation (1) by using the backward finite differences method, Figure 2, produces the final discretised form expressed in Equation (2). The gas concentration was

converted to the unit of partial pressure by assuming that CO₂ obeys the ideal gas behaviour under the operation conditions.

$$p_{CO_2}(z, t) = \frac{[\Delta z \times p_{CO_2}(z, t - \Delta t)] + [u_z \times \Delta t \times p_{CO_2}(z - \Delta z, t)] + [\Delta z \times \Delta t \times R \times T_G \times S_{CO_2}]}{\Delta z + [u_z \times \Delta t]} \quad (2)$$

The initial conditions for Equation (2) are:

$$p_{CO_2}(0, t) = p_{CO_2, initial} \quad t \geq 0 \quad (3)$$

$$p_{CO_2}(z, 0) = 0 \quad z \geq 0 \quad (4)$$

The mole ratio of CO₂ to the inert gas, Y_{CO₂}, is calculated from the partial pressure of CO₂.

$$Y_{CO_2}(z, t) = \frac{p_{CO_2}(z, t)}{p_{tot} - p_{CO_2}(z, t)} \quad (5)$$

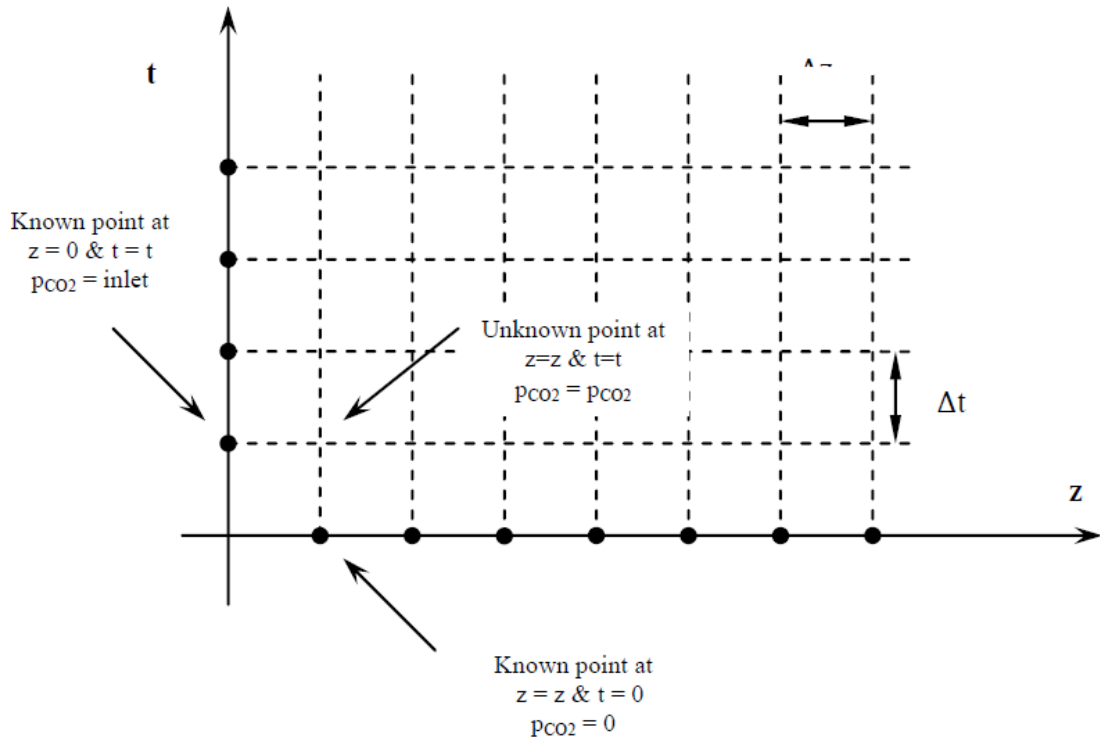


Figure 2. Length-time grids for backward finite difference method.

Liquid-Phase Mass Balance

$$X_{MEA}(z - \Delta z, t) = X_{MEA}(z, t) - \frac{bG_{air}}{L_{water}} [Y_{CO_2}(z, t) - Y_{CO_2}(z - \Delta z, t)] \quad (6)$$

$$C_{MEA}(z - \Delta z, t) = X_{MEA}(z - \Delta z, t) \times \left[\frac{\rho_L}{Mwt_L} \right] x_{water} \quad (7)$$

The general rate equation used to express the reaction rate with respect to the reactor volume as follows (Levenspiel, 1999):

$$S_{CO_2} = \frac{p_{CO_2}}{\frac{1}{k_{CO_2G} a_e} + \frac{H_{CO_2}}{k_{CO_2L} a_e E}} \quad (8)$$

The Henry's constant for CO₂-MEA system is estimated as a function of temperature, T , by using the equation below (Glasscock, Critchfield and Rochelle, 1991).

$$\ln H_{CO_2} = 170.7126 - \frac{8477.711}{T} - 21.9574 \ln T + 0.005781(T) \quad (9)$$

The enhancement factor (E) for the second-order irreversible chemical reaction is evaluated by using the set of equations written below (Wellek and Brunson, 1978).

$$\left[\frac{1}{E - 1} \right]^{1.35} = \left[\frac{1}{E_i - 1} \right]^{1.35} + \left[\frac{1}{E_1 - 1} \right]^{1.35} \quad (10)$$

$$E_i = 1 + \left[\frac{C_{MEA} D_{MEA} H_{CO_2}}{b D_{CO_2} p_{CO_2i}} \right] \quad (11)$$

$$E_1 = \frac{\sqrt{Ha}}{\tanh \sqrt{Ha}} \quad (12)$$

$$Ha = \frac{D_{CO_2} k_2 C_{MEA}}{(k_L)^2} \quad (13)$$

The reaction rate constant is calculated depending on the following relation presented by (Hikita et al, 1979):

$$\log k_2 = 10.99 - \frac{2152}{T} \quad (14)$$

The diffusivity of CO₂ in MEA solution is expressed at different temperatures by using the following equation (Hikita et al, 1979) :

$$D_{CO_2L} = D_{CO_2-water} \left[\frac{1}{\left(\frac{\mu_L}{\mu_{water}} \right)} \right]^{0.8} \quad (15)$$

$$D_{CO_2-water} = 2.35 \times 10^{-6} \exp \left(\frac{-2119}{T} \right) \quad (16)$$

It is seen that the interfacial partial pressure of CO₂ must be known in order to compute the enhancement factor. However, there is no a direct relation by which the interfacial partial pressure can be calculated. Alternatively, it is initially assumed that the interfacial pressure is equal to bulk pressure of CO₂ to calculate the first value of enhancement factor which is then used in Equation (17) to determine the calculated interfacial pressure ($p_{\text{CO}_2\text{i-cal}}$). The later value is introduced back into Equation (11) in order to calculate the second value of the enhancement factor. This procedure should continue until a small difference between the last two values of ($p_{\text{CO}_2\text{i-cal}}$) is met.

$$p_{\text{CO}_2\text{i-cal}} = \frac{p_{\text{CO}_2} + \left[\left(\frac{k_L}{k_G} \right) \times E \times \left(\frac{p_{\text{CO}_2}}{RT_G} \right) \right]}{1 + \left[\left(\frac{k_L}{k_G} \right) \times E \times H_{\text{CO}_2} \right]} \quad (17)$$

Solution Procedures

The model algorithm is shown in Figure 3. The solution procedures start with assuming that the MEA concentration is constant along the length of the absorption column at all times. Following the calculation of the initial value of the enhancement factor, the first attempt to determine the CO₂ partial pressure is made at several time intervals. This is done by solving the gas phase equation using the back ward finite difference method, followed by computing the corresponding concentration curve of the MEA solution by using the liquid phase mass balance equations. These MEA concentration values at different position along the column and at different periods are used then in an inner iteration to find the correct value of the enhancement factor by using Equation (10) through Equation (13). Finally, the corrected enhancement factor is implemented to calculate the reaction rate and then the partial pressure of CO₂. The iteration is carried out until a negligible difference is obtained between two values of MEA concentration at the same position and the same time.

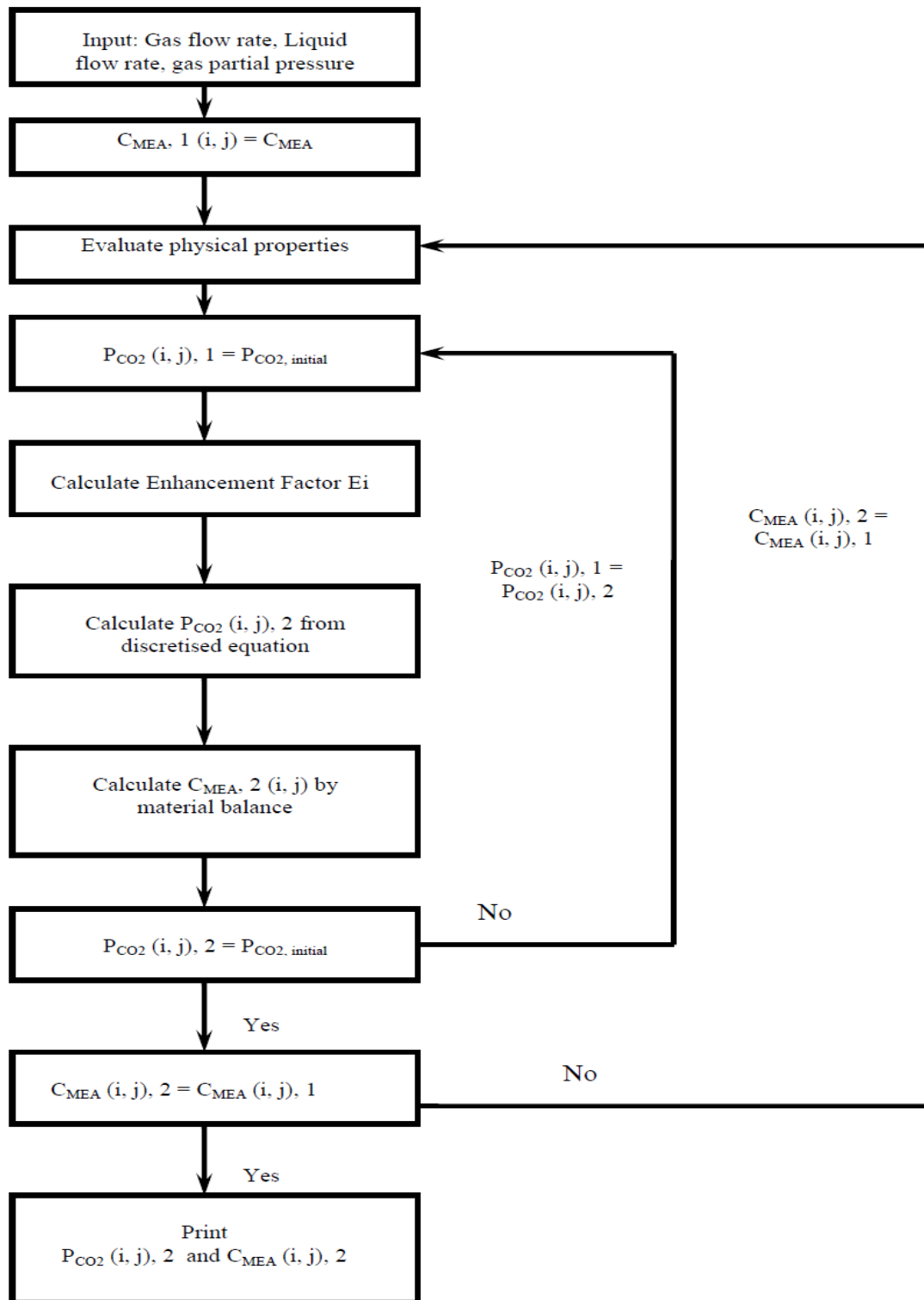


Figure 3. Schematic for the model algorithm

Results and Discussion

The outcomes obtained from the model development are shown and discussed in this part. The results are displayed in terms of figures correlating between changing dependant and independent parameters at several states. Comments will be set for each figure to explain what the most important conclusions are should be highlighted.

Table 1. Specifications of the column absorber

| Parameter | Value |
|--|-------------------------------------|
| Packing Material | Berl Saddles Ceramic |
| Packing size (dp) | 12.7 mm |
| Packing height (Z) | 7 m |
| Effective interfacial area (ae) | 466 m ² / m ³ |
| Surface tension of packing material (σ_C) | 0.061 N/m |
| Packing material constant (c) | 2 |

Model Validation

The experimental measures prepared by Tontiwachwuthikul and others (1992), for steady state CO₂-MEA absorption, is used for validating the model. One experimental run will be taken as a base case and of which changes will be made to simulate other practical cases.

Run 22

Gas flow rate: 14.8 mol/m² s

Liquid flow rate: 9.5 m³/m² s

MEA Initial concentration: 3000 mol/m³

CO₂ Initial partial pressure: 19702 Pa

Figure (4) shows three types of data. The steady state experimental estimations for the CO₂ partial pressure gradient, other steady state simulation model (Khan, 2009), and the other curves clarify the unsteady state predictions. It is seen that the steady state modelling predictions have a good agreement with the experimental ones. The CO₂ partial pressure decreases sharply and linearly from bottom of the column until about 1.5m higher due to the high amount of the gas and then reduces gradually.

The MEA concentration gradient is illustrated in Figure (5). The liquid solution composition remains unchanged for approximately the first three meters beginning from the top after which an exponential drop in MEA concentration occurs. The

deviation is reasonable at the column top but it increases as the liquid solution goes down the column.

It can be noticed from the two figures that the time needed for the unsteady state operation to go finally to the steady state is 60 s which is considered short time period comparing to the time range estimated in the experimental work which is about 30 minutes. This can be interpreted with referring to the assumption of the isothermal operation and subsequently neglecting the thermal influences such as the heat of solution.

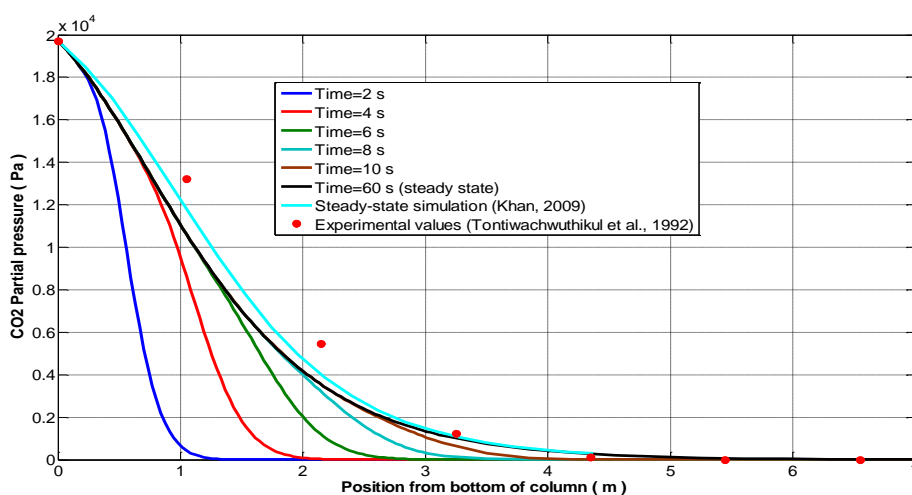


Figure 4. CO₂ Partial pressure profile as a function of the packed column height.

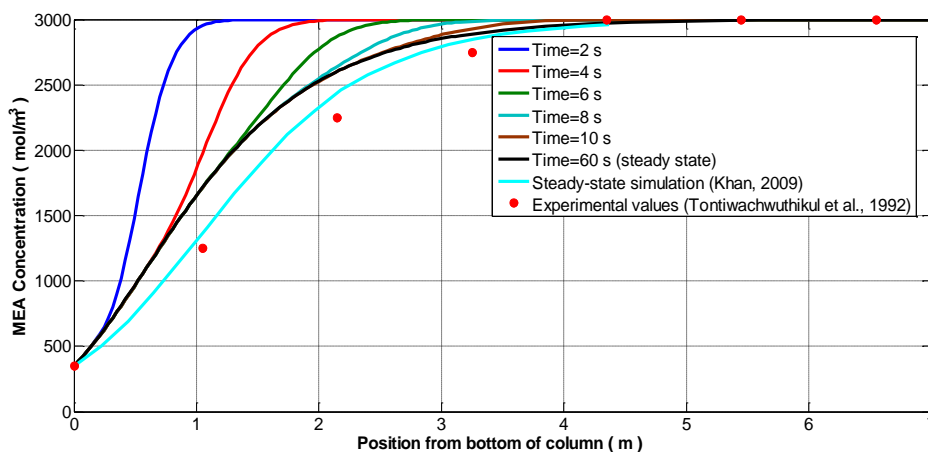


Figure 5. MEA Concentration profile as a function of the packed column height.

Simulation of Practical Cases

The mathematical model should be applied for industrial cases happening truly in order to gain its realistic features. A number of cases, which are speculated occurring during the absorption process operation, will be simulated in this section. No industrial data are available so comparison will be lacked.

Gradual CO₂-Loading Variation. The case which has been studied in this research is the flow rate change after starting-up the operation during which the CO₂-loading varies due to the increase or decrease in the upstream power plant production capacity of the flue gas. The change in the CO₂ concentration is assumed to be gradually rather than suddenly as plotted in Figure 6. The CO₂ loading in the flue gas varies linearly after obtaining the steady state curve for the first operation conditions which begin at CO₂ partial pressure of 19702 Pa and then drops gradually to 15988 Pa and keeps constant until the end of operation time.

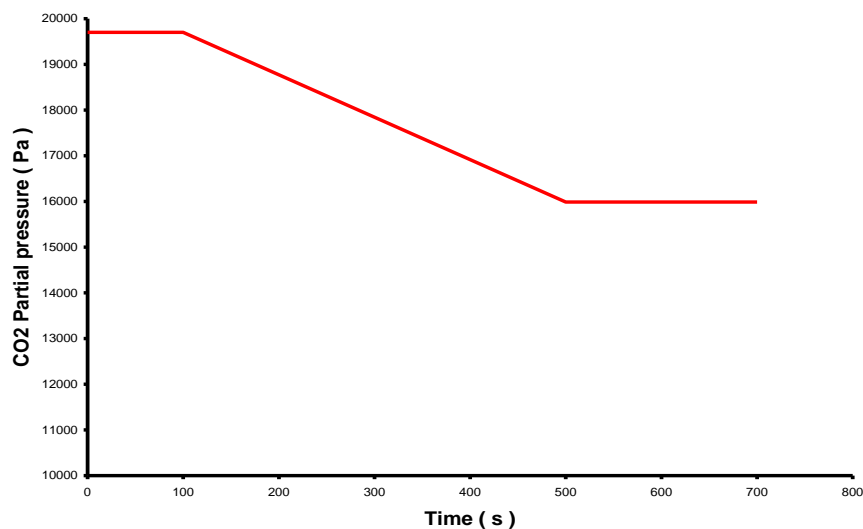


Figure 6. Gradual changes in CO₂ inlet pressure.

This continuous change in the CO₂ concentration results in a continuous varying removing level inside the absorber and no steady state stage is expected to occur until re-obtaining a constant gaseous feed concentration. Figure (7) clarifies more than one curve representing the course of unstable operation. In regarding to the Figure (6), the CO₂ inlet pressure change into the interval from 100 to 500 seconds. During this period the column is distributed as the partial pressure of CO₂ decreases with the gradual decrease of the inlet pressure from 19702 Pa to 15988 Pa. Then, it will re-maintain the steady operation once the inlet pressure is stabilized.

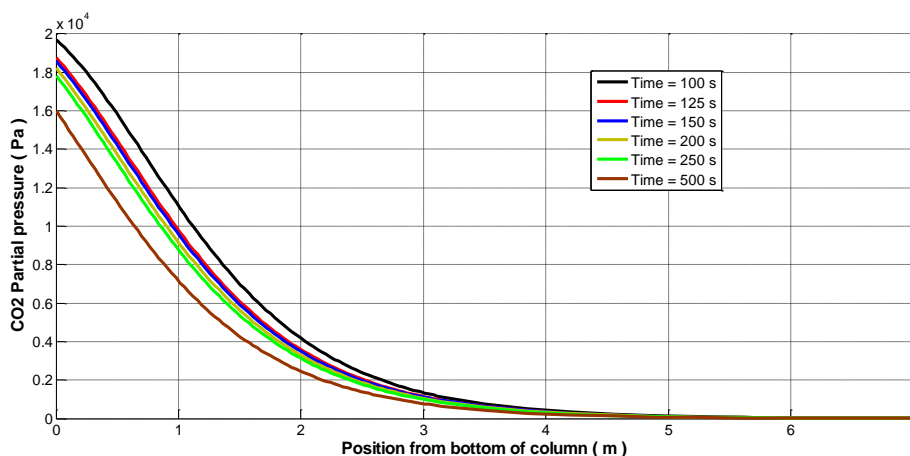


Figure 7. CO₂ Partial pressure gradient with gradual change in the CO₂ inlet partial pressure.

Gas and liquid flow rate variation. The flow rate change has been ignored in the previous cases, while studying the effect of the CO₂ concentration variation on the removal level and the MEA solution concentration gradient. However, power plants are designed to operate with different capacity, which means that the productivity of a plant could be reduced at certain times due to operation requirements. The simulation of a sudden variation in the flow rate is simulated in this section with changing the corresponding flow rate of the liquid solution.

As it is seen in Figure 8, the initial flow rate of the gas stream is 14.8 mol/m² s and changed after reaching the steady state operation to 11.1 mol/m² s, which causes other dynamic operation course before obtaining the new steady state operation. The change in the gas flow rate has been made while operating the column with the same liquid flow rate. The second investigate included the change of the gas flow rate from the original operation conditions (i.e. gas flow rate = 14.8 mol/m² s) to be decreased to 11.1 mol/m² s with an associated decrease in the MEA solution flow rate.

The results are shown below. It is clearly seen that an improvement of the column performance has been achieved when dropping the gas flow rate. However, the column has been dynamically performed for a period of time before stabilising the removal level. In addition, maintaining the same liquid flow rate could cost highly. Therefore, a corresponding alert in the MEA solution flow rate is a significantly effective in such cases to protect the tower from any disturbances and to save the MEA solution costs. As shown in Figure (8), the CO₂ partial pressure has been preserved when the liquid to gas ratio was approximately constant.

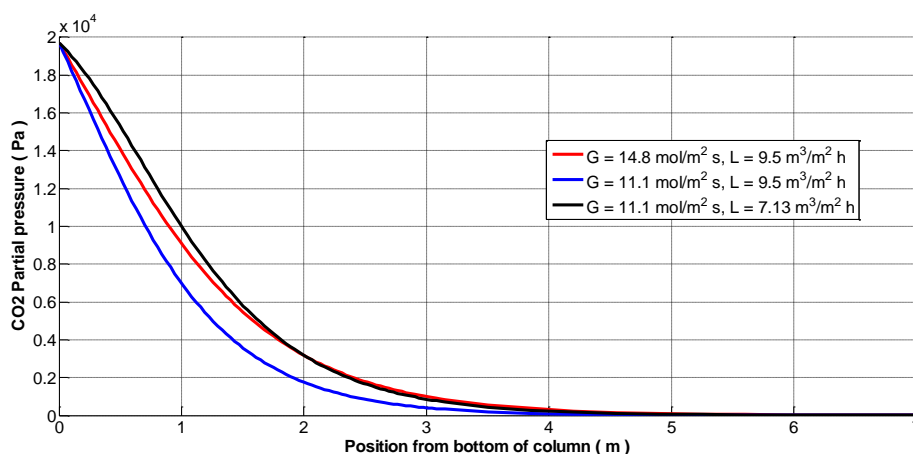


Figure 8. CO₂ Partial pressure gradient at different gas and liquid flow rate

Conclusion

The mathematical model describing the unsteady state behaviour of the CO₂-MEA absorption system in a packed column has been developed. The dynamic model for the packed tower has been prepared based on the model considering the use of a spray tower for removing CO₂ by using MEA. The current model used the conventional unsteady state continuity equation of mass transfer to find the CO₂ concentration profile against the column height during a period of time. The partial differential equation governing the gas-phase mass transfer was solved numerically by using the backward finite difference method. The MEA solvent concentration was then found by material balance. Finally, the set of the system equations were implemented in MATLAB software to be solved. Different scenarios of CO₂ loading variation in the flue gas stream have been considered in order to investigate the column performance at these unordinary conditions.

It was found that the CO₂ removal level is significantly affected by the change of CO₂ loading, which influenced the MEA concentration gradient through the column. In addition, the steady state operation conditions cannot be reached in case of continues change of the CO₂ inlet partial pressure, therefore, the time period through which such changes are made must consider the time needed for steady state and the removal efficiency needed. Furthermore, the MEA/CO₂ is not as effective as the G/L ration which can be considered a controlling factor to maintain the absorber working at the same performance through maintaining constant G/L ratio. The model predicted CO₂ concentrations were in a very acceptable agreement with the published experimental cases, but less harmony was noticed for MEA concentration results.

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