

Modeling and Parametric Investigation of Rotating Packed Bed Processes for CO₂ Capture and Mineralisation

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Rotating Packed Beds (RPB) are receiving increased attention in CO₂ capture, due to their considerably lower volume compared to conventional packed-beds and their beneficial effects on process capital costs. As a result of these advantages, RPB have also been considered as a CO₂ mineralisation option for the production of precipitated calcium carbonate (PCC). In the area of CO₂ capture, the few model-based investigations employ either the two-film or Higbie's penetration theory to model the gas-liquid mass transfer as the main driving force of the systems' operation. In the area of PCC production, there is only one model type available that is based on the two-film theory. While the latter includes the limiting assumption of linear and steady-state mass transfer within the liquid film, Higbie's theory is considerably closer to realistic operation due to the assumption of time-dependent and non-linear, gas-to-liquid mass transfer. Considering this significant advantage, this work proposes for the first time a model for RPB-based, PCC production using Higbie's penetration theory. The model is first developed and validated considering solvent-based CO₂ capture with monoethanolamine (MEA) solvent, taking advantage of the available experimental data in published literature. The model is then adapted to PCC production to perform a parametric investigation based on various performance indicators. Results indicate that the proposed model enables improved accuracy compared to the two film theory. Higher rotation speeds and liquid flowrates enable improved mass transfer, whereas PCC production can be achieved at lower energy consumption simultaneously with high CO₂ capture efficiency.

1. Introduction

The abatement of industrial CO₂ emissions is a key requirement in order to avert the detrimental environmental impacts associated with global warming. Absorption-based CO₂ capture (Bui et al., 2018) and subsequent transformation of CO₂ into carbonated minerals such as precipitated calcium carbonate (PCC) (Jimoh et al., 2018) represent mature and promising technologies for short- to medium-term implementation. There are currently several large-scale pilot plants and two commercial installations of solvent-based absorption processes worldwide (Idem et al., 2015). PCC has a very broad range of applications in building materials, cement, plastics, paper, pharmaceuticals, dyes and represents a very appealing CO₂ utilisation option for carbon leakage industries such as cement, lime, paper and steel (Sargheini et al., 2012). Despite these promising developments, CO₂ absorption is predominantly performed in conventional packed-bed columns (Bui et al., 2018), whereas PCC is produced in continuous stirred-tank (CSTR) reactors, with detrimental effects in both cases on reaction rates, equipment sizes, and, eventually, capital expenditures (Jimoh et al., 2018). Rotating packed beds (Wang et al., 2011) represent a type of intensified equipment that can address all these shortcomings and promises significant size and capital cost reduction (Wang et al., 2015), compared to packed-bed columns and CSTRs. This is because RPBs enable significant enhancement of the mass-transfer rate between the gas and liquid phases (Vlahostergios et al., 2020) as they are contacted in the presence of a high centrifugal field, with beneficial effects on the gas-liquid contact area (Qammar et al., 2018).

Although existing research efforts are predominantly based on experimental works in both the CO₂ capture and PCC production through RPBs (Neumann et al., 2018), model-based approaches are also very useful for process scaling-up. In the area of CO₂ capture there are few published works that focus on the development of

RPB process models and on the effects that different operating parameters have on separation efficiency, carbon capture level and so forth (Borhani and Wang, 2019). Qian et al. (2009) developed a model of the absorption of CO₂ by aqueous N-methyldiethanolamine (MDEA), focusing on modeling the diffusion reaction process by Higbie's penetration theory. The same authors presented a follow-up study on the selective absorption of hydrogen sulfide and CO₂ by MDEA, using the same modelling approach. Sun et al. (2009) presented a model for absorption of CO₂ and ammonia into water in an RPB, based on the two-film theory for reactive gas absorption. A similar modelling approach has been used by Yi et al. (2009) who studied the absorption of CO₂ into a Benfield solution (hot potassium carbonate promoted by diethanolamine) with limited however information about the physical properties utilised in the study. Recently, Borhani et al. (2019) developed a rate-based model using the two-film theory to represent the absorption process of CO₂ in a concentrated monoethanolamine (MEA) solution in an RPB. On the other hand, there is only one report that pertains to modeling of an RPB for PCC (Pan et al., 2015), where the two-film theory was used to investigate the impact of process parameters to conversion efficiency and energetic requirements. The focus was only on the gas-side coefficient, despite the enormous importance of the liquid phase on process performance.

Clearly, Higbie's penetration theory needs to be investigated in PCC production for various reasons. It is closer to operating reality, since it assumes that the mass transfer of the gas into the liquid takes place at unsteady-state conditions (Morsi and Basha, 2015). In the two-film theory, the liquid-side mass transfer coefficient is based on the assumption that the concentration profile is linear and at steady-state within the liquid film, whereas it is non-linear and time-dependent in reality. In Higbie's theory the liquid-side mass transfer coefficient is expressed within a non-linear function of the contact time and of the molecular diffusivity of the gas into the liquid.

This work proposes for the first time a model for PCC production in an RPB, based on Higbie's penetration theory. The Qian et al. (2009) implementation of Higbie's theory on solvent-based CO₂ capture is adopted, whereby an analytical expression is used to model the concentration distribution of CO₂ as a function of time and penetration depth in the liquid film. The proposed implementation also requires knowledge of only the reaction kinetic expressions to calculate the necessary mass transfer coefficient. This is very advantageous compared to the implementation of Pan et al. (2015) of the two-film theory, where multiple, often difficult to track down, properties are necessary to calculate the Reynolds, Schmidt, Grashof, Weber and Froude numbers. The proposed model is first developed and validated for solvent-based CO₂ capture using MEA, due to the ample data available in published literature. It is subsequently used to model PCC production, where it is employed to investigate the process operating performance based on different indicators.

2. Modeling of PCC production using Higbie's penetration theory

2.1 PCC and main reactions

PCC is composed of either fine or very fine nanoparticles that are synthesised either by a carbonation or a solution process after the calcination and hydration reaction of a carbonate rock. The absorption of CO₂ in an aqueous solution of Ca(OH)₂ is primarily achieved by a series of equilibrium reactions that occur in the solution and by the protonation of Ca(OH)₂ expressed as follows:

Overall Chemical Reaction



Carbonic Species and Water Equilibria



Ionic-pair equilibria



Solid-liquid Phase Equilibrium



The hydration of carbon dioxide is detailed in reactions (3)-(6). Reaction (5) is a rapid, reversible reaction taking place in parallel with the fast, pseudo-first-order reversible reaction (1).

2.2 Main theory aspects and model development

Higbie's penetration theory investigates the diffusion of gas into an element of the fluid, as the latter slides over their common interface. As implied by its definition, the basis of this theory lies in the fact that, in unsteady-state mass transfer, the depth of penetration into the exposed boundary is dependent on the time of contact; deeper penetration is achieved in longer contact times (Morsi and Basha, 2015). In the case of an RPB, the intense centrifugal forces result in a sharp change of the concentration of the dissolvable gas into the liquid film, which has a short lifetime on the packing surface due to its continuous renewal. This shorter mean lifetime of the liquid film results in a higher mass transfer coefficient. Considering the above, an RPB model is developed where it is assumed that the concentration of every component changes only in the radial direction, as the circumferential motion can be considered insignificant due to little circumferential diffusion of the liquid (Burns and Ramshaw, 1996). It is assumed that the liquid motion in the RPB does not involve back-mixing, hence the liquid radial flow can be approximated by plug flow (Qian et al., 2009). The liquid flow rate is assumed to be constant due to insignificant increase of the liquid mass as the liquid moves outwards. The pressure drop in the RPB is assumed to be negligible because it is minor compared to the overall system pressure (Yi et al., 2009). Although the absorption reaction of CO₂ is exothermic, the variation on temperatures of both gas and liquid can be neglected. This assumption has been verified experimentally by observing that the temperature difference between the inlet gas and outlet liquid streams is very small (Yi et al., 2009). Investigations focus on steady-state RPB operation, where the gas phase resistance is assumed to be negligible, countercurrent contact between liquid and gas is implemented, laminar film flow is assumed on the packing surfaces and all the reactions occur in the liquid film (Yi et al., 2009). The motion of liquid and gas particles is described by Fick's law of diffusion:

$$N_{CO_2} = D_{CO_2} \frac{dC_{CO_2}}{dx} \Big|_{x=0} = \sqrt{k_{ov} D_{CO_2}} (c_{CO_2,0} - c_{CO_2,eq}) \quad (9)$$

where N_{CO_2} is the mass transfer rate at the gas-liquid interface (kmol/m²s), D_{CO_2} is the diffusivity of CO₂ (m²/s), k_{ov} is the overall reaction rate constant (1/s), $c_{CO_2,0}$ is the concentration of CO₂ at the gas-liquid interface (mol/L) and $c_{CO_2,eq}$ is the equilibrium concentration of CO₂ for the reaction (mol/L). Subsequently, a differential mass balance for the gas phase of CO₂ can be introduced, as follows:

$$k_y a \left(y - \frac{H}{P} \frac{1}{K_2 K_3} \frac{(c_{Ca(OH)_2,tot} - c_{Ca(OH)_2}) c_{HCO_3^-}}{c_{Ca(OH)_2}} \right) 2\pi h R dR = G_{N_2} d\left(\frac{y}{1-y}\right) \quad (10)$$

where y is the mole fraction of CO₂ in the gas (-), $k_y = 0.082 T k_L (P)/(H)$, a is the specific area (m²/m³), H is Henry's constant for absorption of CO₂ into Ca(OH)₂ (-), P is the total pressure of the system (kPa), K_2, K_3 are the equilibrium constants of reactions (2) and (3) (-), $c_{Ca(OH)_2,tot}$ is the bulk concentration of total Ca(OH)₂ at the liquid outlet (mol/L), G_{N_2} is the flow rate of N₂ (m³/s), h is the packing height (m) and R is the geometrical radius (m). Based on the reaction stoichiometry, differential mass balances for HCO₃⁻ and Ca(OH)₂ are also needed:

$$k_L a \frac{P}{H} \left(y - \frac{H}{P} \frac{1}{K_2 K_3} \frac{(c_{Ca(OH)_2,tot} - c_{Ca(OH)_2}) c_{HCO_3^-}}{c_{Ca(OH)_2}} \right) 2\pi h R dR = Q_L d(c_{HCO_3^-}) \quad (11)$$

$$-k_L a \frac{P}{H} \left(y - \frac{H}{P} \frac{1}{K_2 K_3} \frac{(c_{Ca(OH)_2,tot} - c_{Ca(OH)_2}) c_{HCO_3^-}}{c_{Ca(OH)_2}} \right) 2\pi h R dR = Q_L d(c_{Ca(OH)_2}) \quad (12)$$

where $c_{HCO_3^-}$, $c_{Ca(OH)_2}$ are the bulk concentrations of HCO₃⁻ and Ca(OH)₂ in the liquid phase and Q_L is the volumetric flow rate of the liquid (m³/s). The analytical expression of the liquid-side mass transfer coefficient k_L used here is independent of the characteristics of the flow, but is affected by the mean lifetime of the liquid film, the reaction rate constant and the liquid diffusivity of CO₂ (Qian et al., 2009):

$$k_L = \frac{\sqrt{k_{ov} D_{CO_2}}}{\bar{t}} [\bar{t} erf(\sqrt{k_{ov} \bar{t}}) + \frac{1}{\pi k_{ov}} e^{-k_{ov} \bar{t}} + \frac{1}{2k_{ov}} erf(\sqrt{k_{ov} \bar{t}})] \quad (13)$$

where \bar{t} is the mean lifetime of the liquid film (s) and erf is an excess error function. The implementation of Qian et al. (2009) on amine-based CO₂ capture is used a) to validate the model based on the MEA solvent and b) to adapt the model on the PCC production process. By applying the calculated liquid-side mass transfer coefficient k_L , the problem solution is addressed as an initial value problem with ordinary differential equations (ODE-IVP).

3. Results and Discussion

3.1 Validation for CO₂ capture using MEA

The proposed model is validated considering CO₂ absorption in MEA (Liu et al., 2016), due to the availability of modeling and experimental results in published literature. Works that pertain to experimental and model-based assessment of CO₂ absorption in Ca(OH)₂ for the production of PCC focus exclusively on the gas-side mass transfer coefficient, which is not considered in the current implementation of Higbie's penetration theory. The proposed model is validated in Figure 1 against results using the two-film theory (Borhani et al., 2019) and in Table 1 against experimental results (Jassim et al., 2007).

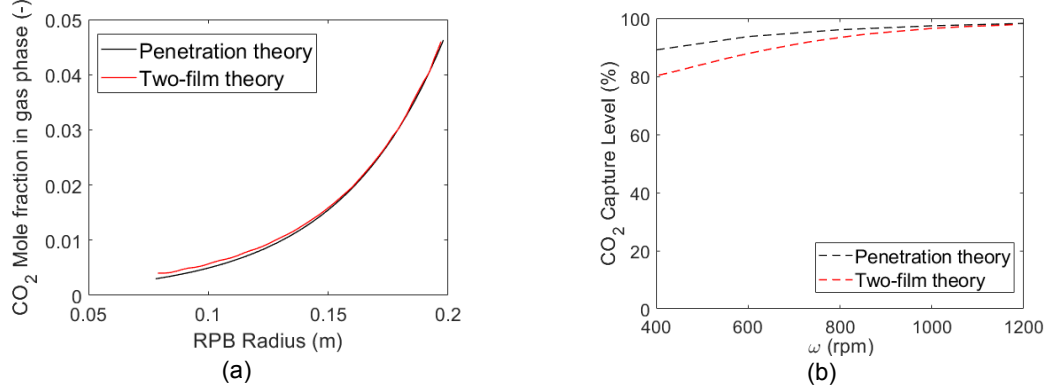


Figure 1: Comparison of a) the CO₂ mole fraction in the gas phase (y_{CO_2}) with respect to the RPB radius, and b) the CO₂ capture level in the RPB with respect to the rotation speed (ω), for MEA between Higbie's penetration theory and the two film theory (Borhani et al., 2019)

As depicted in Figure 1a, the outer radius where flue gas enters the RPB is the point where the highest amount of CO₂ in the flue gas appears. The effect of rotor speed is presented in Figure 1b for the penetration and the two-film theory. The increase of the rotor speed increases the CO₂ Capture Level (CCL). This is due to the improved mass transfer rate that results from increasing the rotor speed. As shown in Figure 1b, the agreement between the two modeling theories is better at higher rotor speeds. In order to gain better insight into the model predictions, error analysis is utilised in this study. The CCL is employed to compare the predicted values from the developed model of this work (penetration theory) with experimental data (Jassim et al., 2007) and predicted values from the two film theory (Borhani et al., 2019). Consequently, the relation of absolute relative deviation (ARD %) is shown in Table 1. ARD % reflects the comparison of the experimental and predicted CCL % values, with the latter calculated based on the outlet $y_{CO_2}^{out}$ and inlet $y_{CO_2}^{in}$ mole fractions of CO₂ in the gas phase.

Table 1: Model prediction results compared to experimental values. $CCL \% = (y_{CO_2}^{in} - y_{CO_2}^{out}) / y_{CO_2}^{in}$ and $ARD \% = |(CCL^{Exp} - CCL^{Pre}) / CCL^{Exp}|$.

MEA wt. (%)	ω (rpm)	Experimental CCL % (Jassim et al., 2007)	Predicted CCL % (Two film theory)	Predicted CCL % (Penetration theory)	ARD % (Two-film theory)	ARD % (Penetration theory)
56	600	94.9	91.0	93.51	4.11	1.46
56	1,000	95.4	97.6	97.30	2.31	1.99
75.1	1,000	91.2	97.05	93.5	6.41	2.52
77	600	84.2	90.06	82.9	6.97	1.54

The proposed model based on Higbie's penetration theory is validated successfully against experimental data. The lower ARD % indicates that the penetration theory is more accurate compared to the two-film theory. The proposed model does not require calculations pertaining to flow characteristics (e.g., Reynolds, Schmidt, Grashof numbers) and to properties such as interfacial area and effective area, that are demanding to determine and there is often a lack of the necessary data.

3.2 Effect of key operating factors on PCC production

The effect of key operating parameters such as the rotation speed (ω) and liquid flow rate (Q_L) on k_L are shown in Figures 2a and 2b for the production of PCC. The k_L values are enhanced with increasing ω (i.e., up to 800–

2,200 rpm) and Q_L (i.e., up to 5.5– 8.5 lt/min), indicating that the mass transfer resistance is reduced in the investigated ranges. The simultaneous implementation of high ω and Q_L is desired to attain high k_L .

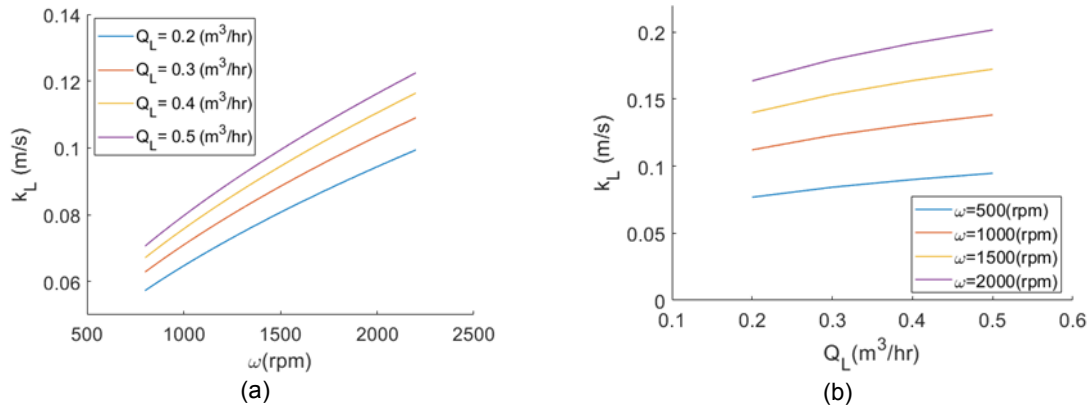


Figure 2: Effect of a) rotation speed (ω), and b) liquid flow rate (Q_L) on k_L for PCC production at $T=313.15$ K

Figure 3a shows the influence of different specific surface areas of packing materials on the CO₂ capture level for different rotation gravity levels (rotation speeds). It appears that a higher specific surface area enables improved capture of CO₂ by the Ca(OH)₂. Figure 3b shows the CO₂ capture level with respect to the RPB radius, for different dissipation energy (ϵ) values. The latter are associated with energy consumption and influence the mixing. Two interesting trade-offs appear here. Lower dissipation energy (slower mixing) enables higher CO₂ capture along the RPB radius, but the dissipation energy is higher (faster mixing) toward the outer radius of the RPB, where the CO₂ capture level is higher. The fast-mixing case ($\epsilon=0.1$ MW/kg) enhances the CCL and reaches the maximum value (98 %) at the outer radius of the RPB. Dissipation energy values of 0.1 MW/kg and 0.01 MW/kg result in a similar performance, especially at the outer RPB end. This means that the same capture level may eventually be achieved with 10 times lower energy consumption. On the other hand, higher capture efficiency may be maintained along the RPB radius at a considerably lower energy rate, if the initially high efficiency within the first few meters is sacrificed.

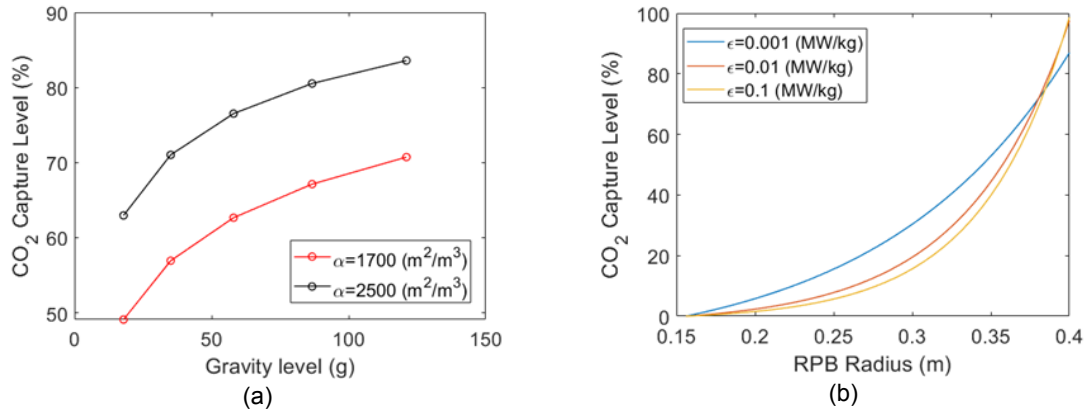


Figure 3: CO₂ capture level against a) gravity level (rotation speed) for different packing specific surface areas (α), and b) RPB radius for different dissipation energies (ϵ) at $\omega = 1000$ rpm. The results are for $Q_L=5.5$ lt/min and the gravity level range corresponds to ω between 400-1,200 rpm

4. Conclusions

The proposed model was validated successfully against experimental data and Higbie's penetration theory was shown to enable improved predictions compared to the two-film theory. The obtained results indicated that the optimum, liquid-side mass transfer coefficient can be reached as the rotation speed and liquid flow rate increase simultaneously. Higher specific surface areas of the packing material enable improved carbon capture efficiency. The latter can also be attained by lower energy consumption, which further enables efficient capture along the RPB radius. The proposed model is reliable in predictions performed for CO₂ absorption in both MEA solvent and Ca(OH)₂. It requires less input data compared to models developed previously based on the two-

film theory, as the calculation of complex flow numbers and properties is avoided. The presented model was implemented only for the liquid phase of the process. It would be worthwhile extending the model toward the gas phase. Although such an extension would enable predictions for all the investigated phenomena, the advantages of the proposed model reported in the manuscript (e.g., the avoidance of the need for gas side transfer coefficients or the need to calculate multiple flow-related numbers) would be abolished. Although isothermal operation was assumed, the attained results were very satisfactory, based on the performed validation.

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