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Modelling and Simulation of CO_2 Absorption in Alkaline Buffer Solutions in gPROMS

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CO_2 capture of from industrial gases is an important and viable strategy for worldwide effort to reduce the human contribution to climate change. Stationary sources of CO_2 as power plants, oil refineries, gas processing plants, cement plants, iron and steel plants basically use fossil fuels as feedstock. The aim of this work is to formulate and validate a mathematical model for the first step (absorption with chemical reaction in $NaHCO_3/Na_2CO_3$ buffer solutions) for CO_2 capture from flue gas with blue-green algae (species *Spirulina*) in fotobioreactors. Physical/mathematical models are developed for a series of continuous stirred tank reactors (CSTR). Gas-liquid mass transfer with chemical reaction, specific to CO_2 – buffer solution $Na_2CO_3/NaHCO_3$ system, is taken into account. Physical/chemical equilibrium/kinetic model parameters (equilibrium constants as well as kinetic constants) are considered to formulate and to implement the model in gPROMS. This model can be reused for process modelling in the second step (CO_2 capture by blue-green algae, species *Spirulina*, in fotobioreactors).

1. Introduction

Global warning associated with increasing greenhouse effect of emissions represents a worldwide major problem due to increasing of fossil fuels combustion. Many engineering problems still need to be solved for developing sustainable production systems to reduce CO_2 emissions. Several techniques are focused on bio-fixation of CO_2 from flue gas through micro-algae (chemical absorption, solid adsorption, carbon molecular sieve adsorption, cryogenic distillation, membrane separation). Novel methods as biological sequestration with different types of algae growing in alkaline solutions are considered as potential alternatives. Power plant flue gas CO_2 (2-10% CO_2) can be absorbed in alkaline buffer solutions (as $Na_2CO_3/NaHCO_3$) to become nutrient for algae, under the influence of natural or artificial light. CO_2 solubilised in water, transformed in the ionized state, is required for all photosynthetic organisms to produce biomass. Additional nutrients such as phosphates, nitrates and ammonia are added to the culture media to meet algae growing needs. Biomass growth can be controlled, to obtain CO_2 biofixation into useful products (proteins, lipids,

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polysaccharides, etc). Separation with specific methods is performed in a later stage. Biotechnological process modelling becomes a challenging task for the development of new CO_2 bio-fixation processes. Numerous studies presented information regarding absorption of CO_2 in alkaline buffer solutions as a gas-liquid mass transfer process involving two step reactions (Danckwerts et al., 1963; Vas Bhat et al., 2000). The influence of liquid physical properties, phase flow and gas injector geometry for bubbling gas type reactors was reported by (Nielsen and Villadsen, 1994). Different studies for both reactions considered as irreversible and instantaneous, or fast and irreversible, or instantaneous and reversible. For example (Lin et al., 2003) considered film or penetration theories for mass transfer. (Takemura and Matsumoto, 2000) demonstrated experimentally and numerically that chemical equilibrium was not achieved at bubble gas-liquid interface. (Taghizadeh et al., 2001) presented the effect of temperature for non-isothermal gas-liquid absorption with chemical reaction and (Alvarez et al., 2008) studied the absorption process taking into account influence of gas and liquid flow rates and bubble size. CO_2 fixation process has two steps: absorption of CO_2 in liquid with favourable pH and biomass production by micro algae photosynthesis, under the influence of light. Many experimental works and correlations are available on this topic but most of them does not concern modeling of absorptions of CO_2 (Vazquez *et al.,* 2000; Vas Bhat at al., 2000; Cents et al., 2001).

In this paper an improved mathematical model of Vas Bhat (Vas Bhat et al., 2000) is proposed for a series of two reactors absorbing CO_2 from flue gas stream (containing 7 % CO_2) in Na_2CO_3/$NaHCO_3$ 5 % buffer solution. Physical model describing CO_2 absorption into buffer solutions is developed assuming solution equilibrium chemistry, overall gas-liquid mass transfer coefficients and continuous stirred reactor mathematical model.

2. Physical Model

In principle, various methods could be used to remove CO_2 from gases, but absorption in liquids is most economic (Vasquez et al., 2000; Cents et al., 2001). Dissolution can be physical or a solute can react with CO_2, at big specific rate of absorption. The process is determined by hydrodynamic conditions (flow rate, column geometry, liquid physical properties, etc) as well as by system physical-chemical properties (solubility of CO_2 in liquid phase, diffusivity of dissolved CO_2 and reactants, reaction kinetics, etc).

Physical model/kinetics model for CO_2 absorption in Na_2CO_3/$NaHCO_3$ buffer solution proposed in this paper considers following phenomena:

a) *Diffusion and physical absorption:* CO_2 Henry's law between CO_2 composition in liquid phase and gas phase respectively

$$C_{CO_2}^{L} = C_{CO_2}^{G} \cdot m \tag{1}$$

b) *Absorption with chemical reaction*: CO_2 mass transfer process can be predicted based on film theory (Chatterjee and Altwicker, 2008). CO_2 absorption in Na_2CO_3/ $NaHCO_3$ buffer solution reaction system is presented in Figure 1. Liquid phase dissolved CO_2 reacts with HO^- ions to form HCO_3^-. All the chemical reactions are assumed to be at equilibrium, while the concentration of water is assumed constant. The concentration of remaining five chemical species, shown in the next chemical reactions, is calculated solving mass balance equations.

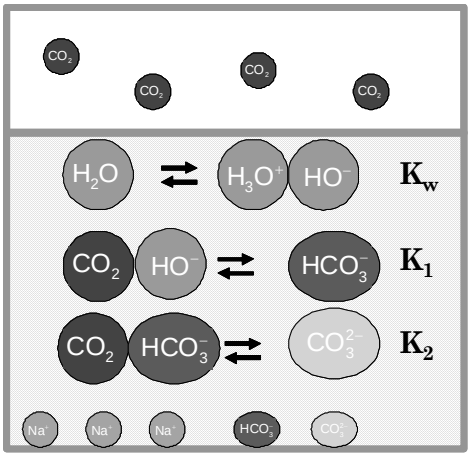

Figure 1 Chemical equilibrium

CO_2 chemical reaction in liquid phase :

$$CO_2 + OH^- \underset{k1,2}{\overset{k1,1}{\rightleftharpoons}} HCO_3^- \qquad \text{(R1)}$$

Ionic chemical reaction:

$$HCO_3^- + OH^- \underset{k2,2}{\overset{k2,1}{\rightleftharpoons}} CO_3^{2-} + H_2O \qquad \text{(R2)}$$

Ionization of water

$$H_3O^- + OH^- \underset{k3,2}{\overset{k3,1}{\rightleftharpoons}} 2H_2O \qquad \text{(R3)}$$

Equations for chemical equilibrium constants are:

$$K_1 \cdot C^{L,e}_{CO_2} \cdot C^{e}_{OH^-} - C^{e}_{HCO_3^-} = 0 \qquad (2)$$

$$K_2 \cdot C^{e}_{HCO_3^-} \cdot C^{e}_{OH^-} - C^{e}_{CO_3^{2-}} = 0 \qquad (3)$$

$$K_w - C^{e}_{H_3O^+} \cdot C^{e}_{OH^-} = 0 \qquad (4)$$

Electrical charge conservation equation for all ionised chemical species in liquid phase:

$$C^{e}_{H_3O^+} + C^{e}_{Na^+} = 2 \cdot C^{e}_{CO_3^{2-}} + C^{e}_{HO^-} + C^{e}_{HCO_3^-} \qquad (5)$$

$$C^{ini}_{Na^+} = C^{e}_{Na^+} \qquad (6)$$

Carbon species conservation equation:

$$\varepsilon \cdot \left(C^{G,ini}_{CO_2} - C^{G,e}_{CO_2} \right) = (1-\varepsilon) \cdot \left(-C^{L,ini}_{CO_2} + C^{L,e}_{CO_2} - C^{e}_{HCO_3^-} - C^{ini}_{CO_3^{2-}} + C^{e}_{CO_3^{2-}} \right) \qquad (7)$$

Where : $\varepsilon = V_G / (V_G + V_L)$, V_G – gas volume, V_L – liquid volume.

CO_2 solubility (in terms of Henry's law constant, *m*) and the equilibrium constants for chemical reactions RI, RII and RIII are required to solve these nonlinear algebraic equations for the species bulk concentration (Vas Bhat et al., 2000, Cents et al., 2005).

3. Mathematical Model

For this study a reaction system with two reactors, and following hypotheses are considered (Iancu et al., 2009): gas and liquid phases are perfectly mixed; for each phase has constant volume in the reactor; secondary phenomena are neglected (water vaporization, liquid phase entrainment, etc); mass transfer resistance in gas phase is neglected ($\delta_G = 0 \Rightarrow k_G \to \infty$); CO_2 concentration is affected by two concurrent processes: gas – liquid mass transfer and CO_2 consumption in chemical reaction; HCO_3^- concentration is affected only by chemical processes : generation is in reaction (1) and consumption is in reaction (2).

The mathematical model for CO_2 absorption consists of mass balances for CO_2, HCO_3^- and CO_2^G chemical species, as follows:

$$\frac{dC^{L}_{CO_2}}{dt} = k_L \cdot a_v \cdot \left(C^{G}_{CO_2} \cdot m - C^{L}_{CO_2} \right) - k_{11} \cdot \left(C^{L}_{CO_2} \cdot C_{HO^-} - \frac{1}{K_1} \cdot C_{HCO_3^-} \right) \qquad (8)$$

Initial condition: t = 0 $C_{CO_2}^{L} = C_{CO_2}^{L,0}$

$$\frac{dC_{HCO_3^-}}{dt} = k_{22} \cdot \left(C_{CO_3^{2-}} - K_2 \cdot C_{HO^-} \cdot C_{HCO_3^-} \right) \tag{9}$$

Initial condition : t = 0 $C_{HCO_3^-} = C_{HCO_3^-}^{equil}$

$$C_{CO_2}^{G,e}(t) = C_{CO_2}^{G,I}(t) - \frac{k_L \cdot a_v \cdot \left(C_{CO_2}^{G,e}(t) \cdot m - C_{CO_2}^{L}(t) \right) \cdot V_L}{G_{gaz}} \tag{10}$$

For all carbon species conservation, the following equation is considered:

$$\frac{d\left(C_{CO_2}^{L} + C_{HCO_3^-} + C_{CO_3^{2-}} \right)}{dt} = \frac{G_{gaz}}{V_L} \cdot \left(C_{CO_2}^{G,I} - C_{CO_2}^{G,e}(t) \right) \tag{11}$$

Initial condition from the above : $t = 0,\ C_{CO_3^{2-}} = C_{CO_3^{2-}}^{\text{equil}}$

Kinetic constants are calculated as presented in literature (Vas Bhat et al., 2000)

4. Simulation of Reactor Model

For validation of mathematical model, two interconnected isothermal stirred tank reactor are considered. These reactors are cylindrical and initially are filled with 300 mL fresh Na_2CO_3 aqueous solution of given composition 5 %, waiting then enough time to get equilibrium under a controlled CO_2 atmosphere at temperature 298 K. At t=0, a constant flowrate bubbling gas stream (40 L/h, 7 % CO_2 and atmospheric pressure) passes from below through the liquid. Based on these assumptions and above mathematical model for absorption of CO_2 in Na_2CO_3/$NaHCO_3$ buffer solution, a composite model is implemented in gPROMS (www.psenterpise.com). The model components are : chemical equilibrium, physical-chemical parameters, kinetic model for one reactor and series of reactors model. Two steps methodology is used for simulation of reactor model: chemical equilibrium model to obtain equilibrium concentrations for all chemical species is solved and then reactor model is solved to predict time profile for chemical species concentration in each reactor.

5. Results and Discussions

A summary of all chemical species concentration at initial state (fresh solution of Na_2CO_3), equilibrium solution (at t=0) and CO_2 saturated solution (after considerable time of flue gas bubbling in the reactor) conditions is presented in Table 1. Mass transfer coefficient k_La is used as parameter, predicted by (Painmanakul et al., 2009). After model solution concentration profiles for all the chemical species are obtained in both reactors. In Figure 2 concentration profiles for the first reactor are presented.

CO_2 concentration in liquid phase, increases until saturation (1.34 mol/m^3). CO_2 concentration in gas phase reaches 2.5 mol/m^3. Solution alkalinity decreases a favorable medium for algae culture being created as presented in Figure 3 for the first reactor.

Table 1: Chemical species concentrations

Conc. mol/m^3	H_3O^+	HO^-	CO_2^G	CO_2^L	HCO_3^-	CO_3^{2-}
Initial state	9.99E-5	9.99E-5	0	0	0	462.24
Equilibrium	1.89E-9	5.25E+0	4.07E-5	2.34E-5	5.3	457.00
Saturation	8.57E-7	1.16E-2	2.5E+0	1.34E+0	667.5	128.49

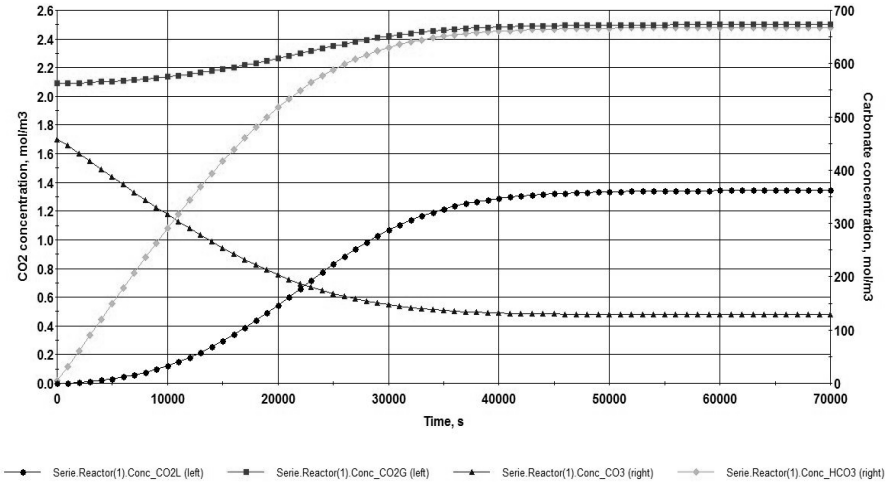

Figure 2: Chemical species concentration profiles (CO_2^G, CO_2^L, CO_3^{2-}, HCO_3^-)

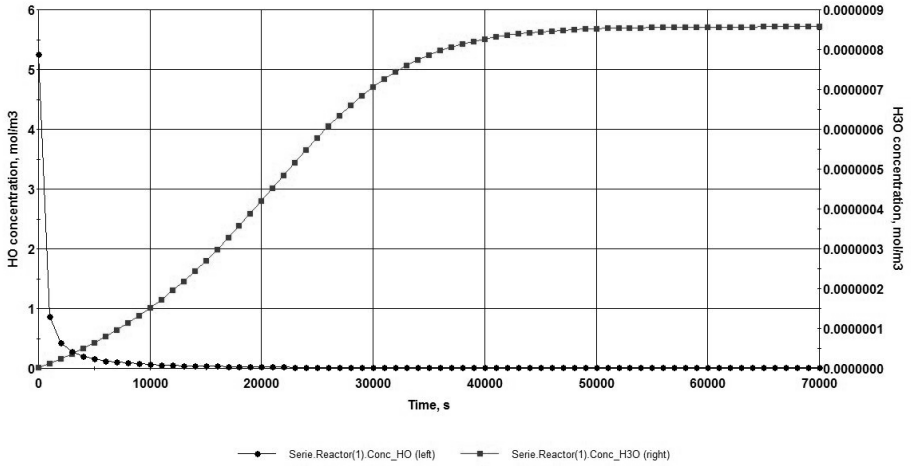

Figure 3: Chemical species concentration profiles (HO^-, H_3O^+)

6. Conclusions

In this paper a mathematical model for CO_2 absorption in Na_2CO_3 / $NaHCO_3$ buffer solutions in a series of two bubble reactors is developed. The model combining hydrodynamics, mass transfer and chemical reaction in bubble column was build as

composite model implemented and solved in gPROMS. The simulation results obtained show realistic behaviour of the proposed model. This can be reused in further investigations for building an extended model for CO_2 capture from flue gas with blue-green algae (species *Spirulina*) in fotobioreactors.

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