MODELLING OF CO_2 MASS TRANSFER AND HYDRODYNAMICS IN A SEMI-BATCH REACTOR

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Abstract

Present study is considered to be a part of modelling the process for removal of CO_2 from industrial gas streams by carbonation of alkaline leachates of oil shale ash formed at Estonian power production. In current paper the chemical phenomena of CO_2 absorption into aqueous alkaline solution has been investigated and a mathematical model for description of CO_2 mass transfer in a stirred semi-batch reactor presented. The model was built upon the kinetics of absorption phenomena as well as reaction kinetics and hydrodynamic conditions. Based on the experimental data and the developed model, the volumetric mass transfer coefficient, k_La of the process was evaluated for a wide range of operating parameters. The model allows simulating the concentration profiles of reactive species and ions (CO_2, CO_3^{2-}, HCO_3^-, OH^-, H^+) in the gas and liquid phase. Additionally, the influence of hydrodynamics on the mass transfer rate of CO_2 was described and empirical functions for estimation of k_La and gas fraction ε in the liquid-gas mixture proposed.

Key words: *absorption, carbon dioxide, mass transfer, hydrodynamics, modelling*

1. INTRODUCTION

Carbon dioxide (CO_2) emissions, inevitably created by burning fossil fuels, are considered the main cause of global climate change. Due to the environmental concerns over greenhouse gas emissions, the removal of CO_2 from industrial gas streams has become especially important (Rubin, ***2001; Weart, 2003).*** Particularly in the Republic of Estonia, where local carbonaceous fossil fuel - oil shale - is used as a ***fuel*** in electricity production, CO_2 emissions reduction is a high priority.

The removal of CO_2 from gas streams can be achieved by a number of separation techniques including absorption into a liquid solvent. Binding CO_2 from flue gases by alkaline wastewaters such as oil shale ash leachates circulating in the hydraulic ash-transportation system at Estonian oil shale firing power plants is a promising method for CO_2 safe disposal. CO_2 mineral trapping based on Estonian oil shale ash and on other lime-containing wastes is a novel approach (Uibu et al., 2009; 2010), which could be economically viable due to availability of large amounts of alkaline wastewater in the proximity of CO_2 emission source. The chemical binding of CO_2 in the form of stable carbonates permits CO_2 emissions reduction as well as utilization of Ca-rich ash alkaline leaching water for precipitated calcium carbonate (PCC) production (Uibu et al., 2010).

However, oil shale ash based PCC production is a complex multistage process, which requires modelling of each stage in order to predict the optimum conditions. In our previous work, the process

of mass transfer of Ca^{2+} ions from oil shale ash particles into aqueous solution was mathematically described (Velts et al., 2010a; 2010b). Nevertheless, vital part of the carbonation process is the transfer of CO_2 from the gas phase to the aqueous phase, since only the dissolved molecules of CO_2 take part in the reactions. However, the data on the rate of CO_2 transfer from air bubbles into the aqueous alkaline solution has rarely been reported in the literature (Astarita, 1963; Danckwerts et al., 1963). Thus, as the next step of the study, present paper aimed to provide an insight into the chemical phenomena of CO_2 absorption into aqueous alkaline solution as well as to develop a mathematical model for predicting mass transfer of CO_2 in a semi-batch reactor, while taking into account the kinetics, hydrodynamics and specifics of the process. Furthermore, the influence of the operating variables such as inlet gas flow rate and CO_2 concentration as well as mixing intensity of the stirrer on the CO_2 mass transfer rate was under attention.

2. MATERIAL AND METHODS

The experiments in a pilot-scale stirred semi-batch reactor were performed by bubbling a gas mixture of CO_2 and air through a recirculating NaOH solution representing the alkaline wastewater (Fig. 1). Gas mixture flow rate and composition was controlled using rotameters and CO_2 analyzer. Reactor was equipped with a gas sampling system connected to CO_2 IR-analyzer (Duotec) to allow measurements of CO_2 concentration in the gas stream exiting the reactor. The pH-value in reactor was continuously monitored by pH meter (Mettler Toledo GWB SG2). Collection of the liquid phase samples was performed by means of sampling valve on the reactor body.

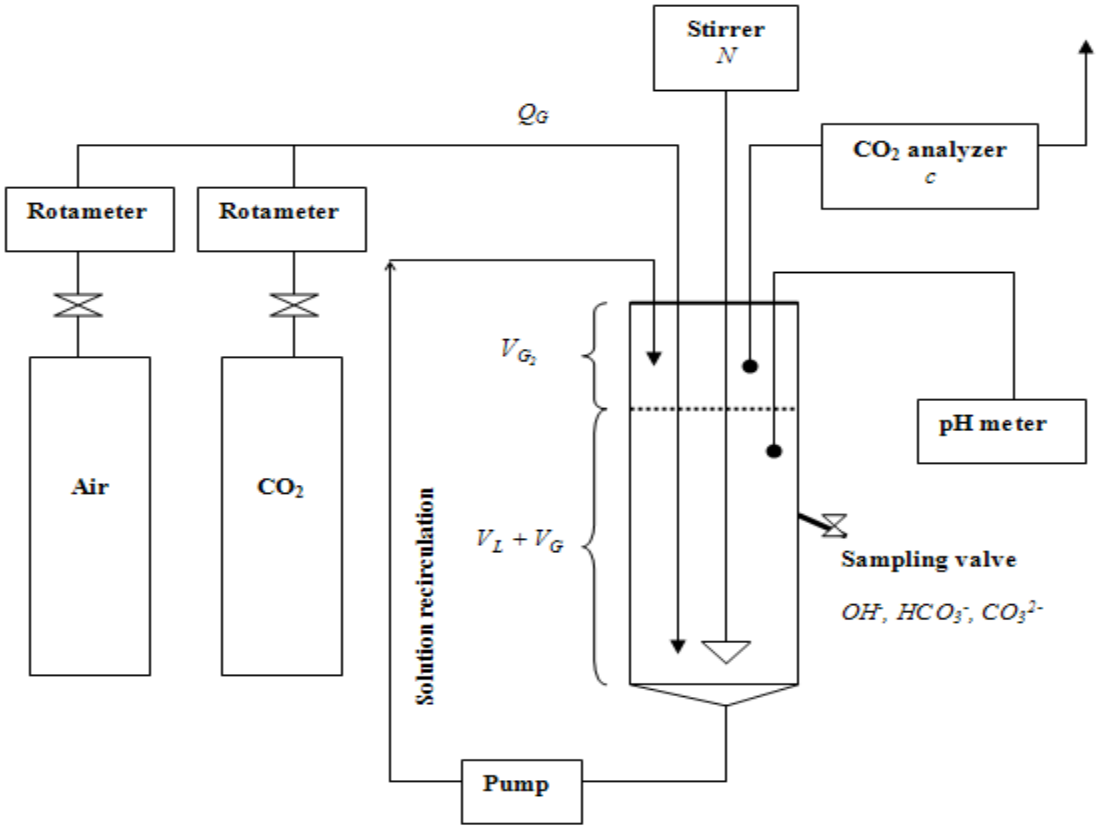


Fig. 1 Principal scheme of the experimental setup

NaOH solution initial volume, concentration and pH were fixed at 10 L, 0.01 M and 12.0 respectively. The pH-level was chosen to be equal to this characteristic for saturated system water − lime containing ash. According to full-factorial experimental plan with additional experimental point in the "middle" (Table 1) the following parameters were varied one at a time while keeping the others constant:

- CO_2-air gas mixture flow rate, Q_G
- CO_2 concentration in the inlet, c
- Stirrer rotation speed, N

Table 1. Experimental plan for investigation of the CO_2 mass transfer

№	**Air/CO_2 flow rate**			**CO_2 concentration in the inlet gas**	**Stirrer rotation speed**
	Total (Q_G, *L/h*)	Air	CO_2	*c, vol. %*	*N, rpm*
1	2000	1700	300	15	1000
2	2000	1700	300	15	400
3	2000	1900	100	5	1000
4	2000	1900	100	5	400
5	1000	850	150	15	1000
6	1000	850	150	15	400
7	1000	950	50	5	1000
8	1000	950	50	5	400
9	1500	1350	150	10	700

In the experiments the pH value, concentration of OH^-, CO_3^{2-}, HCO_3^- ions (titrimetric m***ethod ISO 9963-1:1994(E)***) in the liquid phase as well as CO_2 content in the outflow gas were continuously measured. In each experiment the volume of gas phase in the gas-liquid mixture (V_G) and above it (V_{G2}) was registered. Experiments were conducted until the solution pH reached a value of 7.

3. RESULTS AND DISCUSSION

3.1 Modelling of CO_2 mass transfer in a stirred semi-batch reactor

3.1.1 Distribution of carbonate species in an aqueous solution of hydroxides

Carbon dioxide is a volatile weak electrolyte of great industrial importance. CO_2 is sparingly soluble in an aqueous phase (CO_2 solubility in water is 1.45 g/L at 25°C, 100kPa), however the system is somewhat complex (Lide, 1990-1991; Lower, 1999; Reid et al., 1987). Reaction 1 (R1) represents the process of physical dissolution of gaseous CO_2 into liquid solution:

$$CO_2(q) \leftrightarrow CO_2(l) \quad \text{(R1)}$$

At pressures up to about 5 atm, the solubility equilibrium follows Henry's law:

$$\left[CO_2(l)\right]_{eq} = k_H \times P_{CO_2}, \quad (1)$$

where k_H is the Henry constant, Pco_2 is the CO_2 partial pressure.

Once CO_2 has dissolved, equilibrium is established between the dissolved CO_2 and forming carbonic acid. Furthermore, rate of dissolution of CO_2 into water depends on pH with formation of CO_3^{2-} and HCO_3^- ions. Therefore, the reactions occurring during absorption of CO_2 into aqueous solutions of hydroxides can be expressed as follows (Cents et al., 2005):

$$CO_2(l) + OH^- \underset{k_{12}}{\overset{k_{11}}{\rightleftarrows}} HCO_3^- \quad \text{(R2)}$$

$$HCO_3^- + OH^- \underset{k_{22}}{\overset{k_{21}}{\rightleftarrows}} CO_3^{2-} + H_2O \quad \text{(R3)}$$

$$OH^- + H^+ \underset{k_{32}}{\overset{k_{31}}{\rightleftarrows}} H_2O \quad \text{(R4)}$$

$$CO_2(l) + H_2O \underset{k_{42}}{\overset{k_{41}}{\rightleftarrows}} HCO_3^- + H^+ \quad \text{(R5)}$$

Accordingly, the overall concentration of dissolved carbon increases together with the amount of the HCO_3^- and CO_3^{2-} ions formed. Dissolved CO_2 consists thus of the three species:

$$C_{CO_2} = [CO_2(l)] + [HCO_3^-] + [CO_3^{2-}] \quad (2)$$

Therefore, when CO_2 gas is bubbled through a solution containing a strong base such as NaOH, the electro-neutrality balance (in molar concentration units) for such a mixture can be written as follows:

$$[H^+] + [Na^+] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] \quad (3)$$

3.1.2 Estimation of the volumetric mass transfer coefficient k_La for CO_2

Based on the above considerations, the applicability of reactions (R1) - (R5) to describe CO_2 mass transfer from gas phase into the aqueous solutions of sodium hydroxide was studied. In addition to kinetics of the reactions taking place in the liquid phase, the modelling procedure accounted for kinetics of absorption phenomena as well as hydrodynamic conditions of the process.

When CO_2 is bubbled through a perfectly mixed aqueous alkaline solution, the CO_2 mass transfer process can be modelled according to our proposal by the following differential equations for the different species, assuming that the volume remains essentially constant, and that the system is operated isothermally at 25° C:

- *For CO_2 dissolved in water:*

$$\frac{d[CO_2(l)]}{dt} = \frac{k_L a \times \sum_{i=1}^{n} \left(\left(\frac{k_H \times M_{CO_2} \times P \times [CO_2^i(g)]}{\rho_{CO_2}} - [CO_2(l)] \right) \times \frac{V_L + V_G}{n} \right)}{V_L} - k_{11}[CO_2(l)][OH^-] + k_{12}[HCO_3^-] - k_{41}[CO_2(l)] + k_{42}[HCO_3^-][H^+] \quad (4)$$

- *For OH^-, HCO_3^-, CO_3^{2-} and H^+ ions:*

$$\frac{d[OH^-]}{dt} = -k_{11}[CO_2(l)][OH^-] + k_{12}[HCO_3^-] - k_{21}[HCO_3^-][OH^-] + k_{22}[CO_3^{2-}] + k_{32} - k_{31}[OH^-][H^+] \quad (5)$$

$$\frac{d[HCO_3^-]}{dt} = k_{11}[CO_2(l)][OH^-] - k_{12}[HCO_3^-] - k_{21}[HCO_3^-][OH^-] + k_{22}[CO_3^{2-}] + k_{41}[CO_2(l)] - k_{42}[HCO_3^-][H^+] \quad (6)$$

$$\frac{d[CO_3^{2-}]}{dt} = k_{21}[HCO_3^-][OH^-] - k_{22}[CO_3^{2-}] \quad (7)$$

$$\frac{d[H^+]}{dt} = k_{32} - k_{31}[OH^-][H^+] + k_{41}[CO_2(l)] - k_{42}[HCO_3^-][H^+] \quad (8)$$

- *For CO_2 exiting the* ith *section of the reaction mixture:*

$$\frac{d[CO_2^i(g)]}{dt} = \left(\begin{array}{l} Q_G([CO_2(g)]_{IN} - [CO_2^i(g)]) - \\ k_L a \left(\frac{k_H \times M_{CO_2} \times P \times [CO_2^i(g)]}{\rho_{CO_2}} - [CO_2(l)] \right) \times \frac{(V_L + V_G)}{n} \end{array} \right) \Big/ \frac{V_G}{n} \quad (9)$$

- *For CO_2 exiting the reactor e.g. headspace V_{G2} above the reaction mixture* (see Fig. 1):

$$\frac{d[CO_2(g)]_{OUT}}{dt} = (Q_G([CO_2(g)] - [CO_2(g)]_{OUT}))/V_{G_2} \quad (10)$$

In equations (4) - (10) molar concentrations are used. Q_G is the gas volumetric flow rate, L/s; k_La is the volumetric mass transfer coefficient, s^{-1}; V_L is the water volume, L; V_G is the gas volume in the gas-liquid mixture, L; V_{G2} is the gas volume in the empty space above the reaction mixture, L; k_H is the Henry's constant, mol L^{-1} atm^{-1}; P is the atmospheric pressure, atm; M_{CO2} is the CO_2 molar mass, g/mol; ρ_{CO2} is the CO_2 gas density, g/L.

The gas phase in the reaction mixture was divided into a number of theoretical sections n with a volume V_G/n (***gas phase*** in close to the ***plug flow regime,*** liquid phase in the ***perfectly mixed flow regime as solution was recirculated***). Each of these sections (high correlation coefficient observed at n=10) was treated as a non-equilibrium stage, governed by the equation 9.

The value of the Henry's constant, k_H (mol L^{-1} bar^{-1}) was determined as a function of temperature, T (K) from the relation (Pohorecki and Moniuk, 1988):

$$\log k_H = 9.1229 - 5.9044\times10^{-2}T + 7.8857\times10^{-5}T^2 \quad (11)$$

The rate constant k_{11} of reaction 2 (R2) has been correlated as a function of temperature and ionic strength by Pohorecki and Moniuk (Pohorecki and Moniuk, 1988). However, considering near to infinite dilution ionic strength of the 0.01 M NaOH solution, the value of the second-order rate constant k_{11} (L mol^{-1} s^{-1}) can be calculated as only a function of temperature from a relationship (Pohorecki and Moniuk, 1976):

$$\log k_{11} = 11.916 - \frac{2382}{T} \quad (12)$$

The backward reaction rate of reaction 2 (R2), k_{12}, is defined by the value of the equilibrium constant for this reaction ($k_{12}=k_{11}K_w/K_1$). K_1 (mol/m^3) is given as a function of temperature by Edwards et al. (Edwards et al., 1978):

$$K_1 = \exp\left(-\frac{12092.1}{T} - 36.786\ln(T) + 235.482\right)\rho_w, \quad (13)$$

where ρ_w is the density of water (kg/m^3). The value of the solubility product K_w (mol^2/m^6) is given by Tsonopoulos (Tsonopoulos, 1976):

$$\log\left(\frac{K_w}{\rho_w^2}\right) = -\frac{5839.5}{T} - 22.4773\log(T) + 61.2062 \quad (14)$$

Reaction 3 (R3) is fast as it involves only a proton transfer. The reaction rate constant, k_{21}, was determined to be 6×10^6 m^3 mol^{-1} s^{-1} (Eigen, 1963). The equilibrium constant K_2 (m^3/mol) at infinite dilution that determines the value of the backward reaction of reaction 3 (R3), $k_{22}=k_{21}/K_2$, is given by Hikita et al. (Hikita et al., 1976):

$$\log(K_2) = \frac{1568.9}{T} - 2.5866 - 6.737\times10^{-3}T \quad (15)$$

The neutralization rate constant, k_{31}, was determined by Eigen (Eigen, 1963) to be 1.4×10^8 m^3 $mol^{-1}s^{-1}$. The reaction rate between CO_2 and water, k_{41}, is very slow (0.024 s^{-1}, Danckwerts and Sharma, 1966). The values of the backward reactions, k_{32} and k_{42} can be calculated from the equilibrium constants and are k_{31}/K_W and k_{41}/K_1, respectively.

Values of the reaction rate constants used in this paper (T=298.15K) in the modelling of CO_2 absorption are summarized in Table 2.

Table 2. Values of the parameters for absorption of CO_2 in a NaOH solution at 298K

Parameter	k_{11}, $\frac{L}{mol \times s}$	k_{12}, s^{-1}	k_{21}, $\frac{L}{mol \times s}$	k_{22}, s^{-1}	k_{31}, $\frac{L}{mol \times s}$
Value	8.4×10^{3}	2.0×10^{-4}	6.0×10^{9}	1.2×10^{6}	1.4×10^{11}
Parameter	k_{32}, $\frac{mol}{L \times s}$	k_{41}, s^{-1}	k_{42}, $\frac{L}{mol \times s}$	k_H, $\frac{mol}{L \times atm}$	ρ_{CO2}, $\frac{kg}{m^3}$
Value	1.3×10^{-3}	2.4×10^{-2}	5.7×10^{4}	3.5×10^{-2}	1.8

In this paper, the volumetric mass transfer coefficient, k_La, was determined numerically from the differential equations (4) - (10) using the least squares method. The set of model equations were solved by means of linear multi-step methods implemented in ODESSA, which is based on the LSODE software (Hindmarsh, 1983). The calculations were performed using the MODEST 6.1 software package (Haario, 1994) designed for various tasks of model building such as simulation, parameter estimation, sensitivity analysis and optimization. The software consists of a FORTRAN 95/90 library of objective functions, solvers and optimizers linked to model problem-dependent routines and the objective function.

Estimated values of k_La (R^2> 90 %) with their 95% confidence intervals are presented in Table 3 for various absorption conditions in compliance with experimental plan presented in Table 1.

Table 3. Estimated values of volumetric mass transfer coefficient for various absorption conditions

Air/CO_2 flow rate, *L/h*	***CO_2 concentration in the inlet gas,*** *vol. %*	***Stirrer rotation speed,*** *rpm*	***k_La,*** s^{-1}
2000	15	400	$3.27 \pm 0.09 \times 10^{-2}$
2000	15	1000	$4.87 \pm 0.90 \times 10^{-2}$
2000	5	1000	$4.07 \pm 0.25 \times 10^{-2}$
2000	5	400	$2.92 \pm 0.08 \times 10^{-2}$
1000	15	1000	$3.34 \pm 0.21 \times 10^{-2}$
1000	15	400	$2.68 \pm 0.01 \times 10^{-2}$
1000	5	1000	$3.71 \pm 0.14 \times 10^{-2}$
1000	5	400	$1.94 \pm 0.07 \times 10^{-2}$
1500	10	700	$3.23 \pm 0.21 \times 10^{-2}$

The verification of the model was carried out by comparing the simulated and experimental concentration profiles and, in general, a good agreement between them was found.

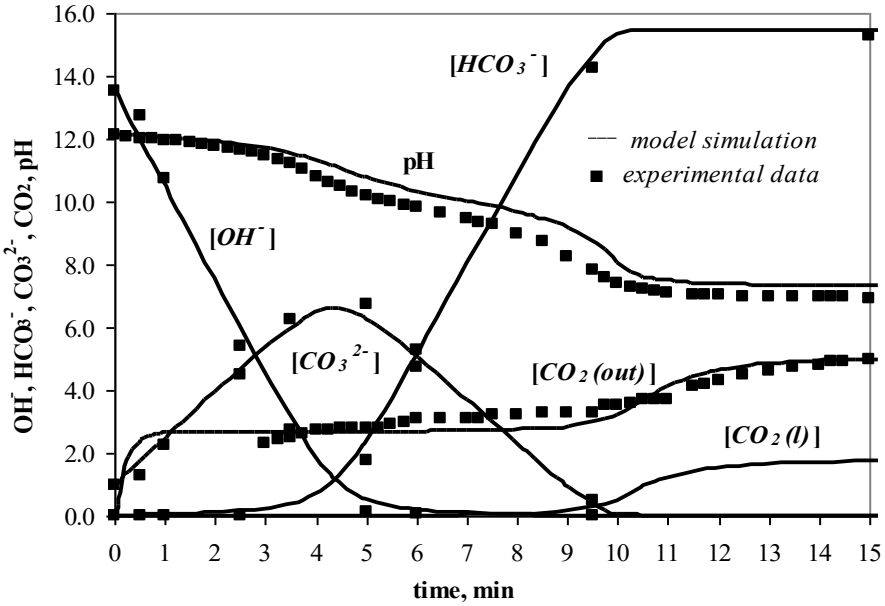


Fig. 2 Modelling of CO_2 absorption at Q_G = 1000 L/h, N = 400 rpm, c = 5%: experimental (■) vs. simulated (—) OH^-, HCO_3^-, CO_3^{2-}, $CO_2(l)$ (mmol/L), $CO_2(out)$ (%) concentration and pH profiles

Examples of the plots of experimental and simulated concentration profiles of the reactive species and ions (CO_2, CO_3^{2-}, HCO_3^-, OH^-) in the gas and liquid phase are shown in Figures 2-4 for various conditions of CO_2 absorption.

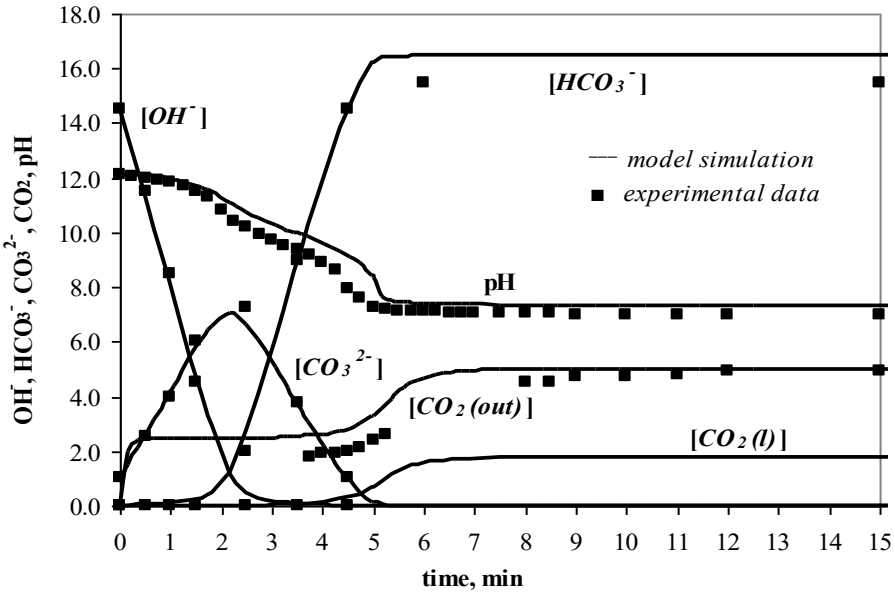


Fig. 3 Modelling of CO_2 absorption at Q_G = 2000 L/h, N = 1000 rpm, c = 5%: experimental (■) vs. simulated (—) OH^-, HCO_3^-, CO_3^{2-}, $CO_2(l)$ (mmol/L), $CO_2(out)$ (%) concentration and pH profiles

Developed model allows also the prediction of pH during the neutralization of NaOH solution as graphically represented by Figures 2-4.

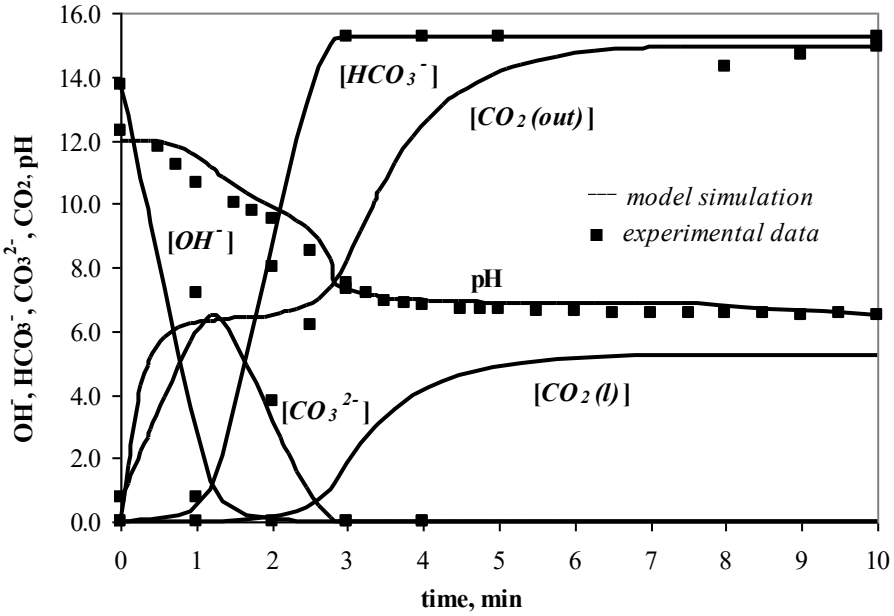


Fig. 4 Modelling of CO_2 absorption at Q_G = 1000 L/h, N = 400 rpm, c = 15%: experimental (■) vs. simulated (—) OH^-, HCO_3^-, CO_3^{2-}, $CO_2(l)$ (mmol/L), $CO_2(out)$ (%) concentration and pH profiles

The results show (see Figures 2-4 above) that the model equations correspond to the experimental data quite well. Thus, the developed model is able to accurately predict the performance of CO_2 absorption into alkali aqueous model solutions in a stirred semi-batch reactor.

3.2 The effects of hydrodynamics and CO_2 partial pressure on the rate of CO_2 mass transfer

The rate of CO_2 transfer (under the conditions prevailing in the reactor) is governed by the liquid phase mass transfer coefficient, k_L and is usually characterized by the volumetric mass transfer coefficient, k_La. A number of equipment and operational parameters interact to influence the efficiency and rate of CO_2 transfer. Hydrodynamic conditions of the process such as gas flow rate and stirrer rotation speed, can be viewed as the main factors affecting the rate of CO_2 mass transfer. These parameters determine factors such as bubble size, degree of turbulence etc. Clearly, another parameter affecting the CO_2 mass transfer performance is the CO_2 concentration in the inlet gas (e.g. CO_2 partial pressure). Increasing the input values of the named operating parameters is known to enhance the mass transfer rate.

As it may be observed from Table 3, the behavior of the volumetric mass transfer coefficient, k_La of CO_2 is in good agreement with the latter statement. Within the ranges of variables studied, it was observed that the mixing speed had the greatest effect on the mass transfer coefficient followed by the gas flow rate. Furthermore, based on the collected data, an empirical correlation (R^2=90%) for estimation of the volumetric mass transfer coefficient k_La (s^{-1}) of carbon dioxide was built up as a function of the operating variables:

$$k_L a = 9.6218 \times 10^{-5} \times N^{0.4316} Q_G^{0.3840} c^{0.1117}, \quad (16)$$

where Q_G is the gas flow rate, L/h; N is the stirrer rotation speed, rpm; c is CO_2 content in the inlet gas, vol. %.

The effect of the stirring speed, gas flow rate and CO_2 partial pressure on the neutralization of NaOH is demonstrated by the experimental pH plots presented in Fig. 5.

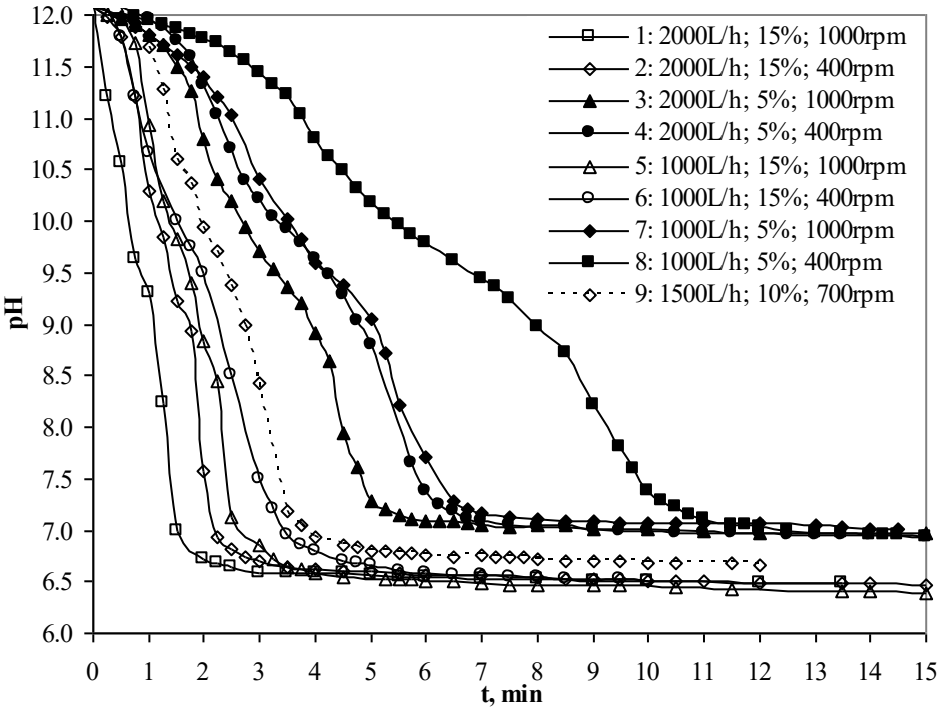


Fig. 5 The experimental pH plots for various conditions of CO_2 absorption

Examination of the curves 1-9 in Fig. 5 shows that the pH value corresponding to a neutral solution ($6.5 < \boldsymbol{pH < 7.0}$) is reached in a shorter time as at least one of the operational variables Q_G, N or c is increased. Furthermore, increasing the stirring speed to 1000 rpm (curve 7) or the gas flow rate to 2000 L/h (curve 4) from the lower boundary conditions, characterized by the curve 8, resulted in a similar pH neutralization performance accompanied by a time reduction of about 4 minutes. In the experiments conducted in the upper boundary conditions of the CO_2 partial pressure, neutral pH region was reached after 3.5 minutes. Combined effect of the simultaneous increase of all three operating variables is demonstrated by the curve 1, whereas pH level 7.0 is reached in about 1.5 minutes.

Clearly, the decrease in CO_2 partial pressure elongates the duration to reach neutral pH, which can be compensated to some extend through the increase of gas flow rate or mixing intensity of the stirrer. Therefore, curve 9 represents the optimum conditions of operating. However, based on the collected data, the appropriate conditions (gas flow rate, stirrer rotation speed, CO_2 partial pressure, process time, etc) can be nevertheless selected depending on the objective of the absorption process (wastewater neutralization, carbonation/precipitation, gas purification) as well as equipment specifics.

It is also worth noting, that the volumetric ratio between the gas and liquid phases in the reaction mixture is mostly determined by the input value of the gas flow rate and stirring speed. Consequently,

empirical function (R^2=99%) for estimation of the gas fraction ε in the liquid-gas mixture was constructed as presented below:

$$\varepsilon = 2.047 \times 10^{-5} \times N^{0.579} Q_G^{0.630} \quad (17)$$

4. CONCLUSION

In this paper, the conditions of experimental work and the results of modelling of CO_2 absorption process into aqueous alkaline solution in a semi-batch reactor have been presented. For the conditions studied, a mathematical model was developed to simulate, design and optimize the CO_2 absorption process. The model includes information on all of the main factors involved in mass transfer of CO_2 from the gas to the liquid phase and the subsequent reactions (e.g. hydrodynamics, kinetics etc). Based on the experimental data and CO_2 mass transfer model, estimation of the volumetric mass transfer coefficient, k_La, was made under different conditions of gas flow rate, mixing speed and initial CO_2 partial pressure. Finally, an empirical correlation for the volumetric mass transfer coefficient of carbon dioxide was proposed as a function of the main operating variables, allowing estimation of absorption performance per unit volume of gas-liquid mixture in the reactor.

As the concentrations of the various carbonate species depend on the pH of the solution, the results of this study lead to a better understanding of the chemistry and specifics of the CO_2 mass transfer process into the alkaline wastewaters such as leaching waters of oil shale ash and other lime-containing waste materials. In the next step of the study the CO_2 mass transfer model described here will be combined with models of calcium carbonate precipitation reaction taking place in heterogeneous gas-liquid-solid system. Furthermore, volumetric mass transfer coefficients, k_La evaluated in this paper, will be used to estimate the enhancement factor due to chemical reaction.

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