ELSEVIER

Chemical Engineering Journal 116 (2006) 203–209

Chemical Engineering Journal

www.elsevier.com/locate/cej

Analysis of mass transfer in the precipitation process of calcium carbonate using a gas/liquid reaction

Diego Gómez-Díaz*, José M. Navaza*, Begoña Sanjurjo

Department of Chemical Engineering, ETSE, University of Santiago de Compostela, Lope Gómez de Marzoa s/n, E-15782, A. Coruña, Spain

Received 20 April 2004; received in revised form 29 November 2005; accepted 7 December 2005

Abstract

Nowadays a typical method to produce calcium carbonate is based on the gas–liquid reaction between carbon dioxide and aqueous solutions of calcium hydroxide. Several chemical engineering processes are involved in this operation, such as mass transfer, chemical kinetics, etc. The aim of this research work is to study the global reaction process that involves absorption, reaction and precipitation processes. The effect of the precipitation process upon the gas/liquid mass transfer operation has been analyzed and the experimental results have shown a clear influence. Also, the characteristics of the solid phase precipitated have been determined and the effect of the reactive system upon these characteristics has been explained.

Keywords: Precipitation; Gas; Carbonate; Transfer

1. Introduction

The development of different methods to remove the pollutant gases emitted by chemical industries has been very important in the last few decades. The mass transfer processes have played an important role in the industrial processes for removal of contaminant gases, such as the use of aqueous solutions of amines to remove carbon dioxide [1]. The evolution of industrial processes towards a minimization of waste generated has provoked the designing of new strategies related to the reusability of the produced wastes. For gas contaminants, the use of these compounds in other processes allows to prevent their direct emission into the atmosphere and the subsequent acid deposition.

For example, one of these procedures is the industrial production of calcium carbonate that is obtained in batch reactors by carbonation route at high temperatures (30–70 °C). Calcium carbonate is obtained directly from nature or it is produced using the reaction between sodium carbonate and calcium hydroxide. The former method consists of bubbling CO_2 gas through an aqueous slurry of $Ca(OH)_2$ or slaked lime [2].

Calcium carbonate exists as three polymorphs (calcite, aragonite and vaterite) with different characteristics, and one of them will be the most appropriate compound for a finite use. Among the different polymorphs of calcium carbonate ($CaCO_3$), calcite is of great interest because of its wide use as a pigment or as a filler in plastics, rubber, paper, paints, etc.

Due to the reduction in the concentration of ions present, the process can be monitored by the measurement of electrical conductivity (κ) of the aqueous suspension during the whole carbonation process [3]. Also, the use of the hydroxyl ions from the calcium hydroxide dissociation for the calcium carbonate production allows the study of the reactive process on the basis of the pH values [4].

We studied the method based on the gas/liquid reaction between carbon dioxide and calcium hydroxide for the calcium carbonate production (Fig. 1). Absorption processes involve a great number of operations. The mass transfer rate is related to several operational variables, such as gas and liquid flowrates, stirring rate, operation temperature, etc. Important factors in this kind of processes are geometrical characteristics of the contact device used to carry out the gas/liquid reaction. The gas/liquid equipment is very common in different industrial operations as fermentors and also for waste-water treatment.

These reasons suggest that the characterization of all processes involved in the global reactive system is necessary. The reaction kinetics of the process is well known and the mecha-

---

* Corresponding authors. Tel.: +31 4564564564; fax: +31 981595012.
E-mail addresses: eqnava1@usc.es (D. Gómez-Díaz), eqnavaza@usc.es (J.M. Navaza).

1385-8947/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2005.12.004

Nomenclature

a	interfacial area (cm^2)
C	CO_2 concentration ($mol\,dm^{-3}$)
$C^*_{CO_2}$	CO_2 solubility ($mol\,dm^{-3}$)
$C^{bulk}_{OH^-}$	OH^- concentration in the bulk of the aqueous phase ($mol\,dm^{-3}$)
$C^{*,solution}_{CO_2}$	CO_2 solubility in the aqueous solution ($mol\,dm^{-3}$)
$C^{*,water}_{CO_2}$	CO_2 solubility in water ($mol\,dm^{-3}$)
D_A	CO_2 diffusivity in the liquid phase ($cm^2\,s^{-1}$)
D_B	OH^- diffusivity in the liquid phase ($cm^2\,s^{-1}$)
i_+, i_-, i_g	contributions of positive ions, negative ions and solute gas to the salting out parameter ($dm^3\,mol^{-1}$)
I	ionic strength ($mol\,dm^{-3}$)
k_2	second-order rate constant ($dm^{-3}\,mol^{-1}\,s^{-1}$)
k_L	liquid side mass transfer coefficient ($cm\,s^{-1}$)
K_S	the salting-out parameter ($dm^3\,mol^{-1}$)
N	rate of absorption ($mol\,dm^{-3}\,s^{-1}$)
Q_g	gas flowrate ($L\,h^{-1}$)
t	operation time (s)
z	stoichiometric coefficient of the overall reaction

nism is shown below [5]. Since the global reaction rate is very fast, the contactor and the values of operational variables can be so chosen that the mass transfer process will be the slowest step. This point of view shows the importance of the equipment design.

$$CO_2\,(g) \leftrightarrow CO_2\,(aq) \tag{A}$$

$$CO_2\,(aq) + OH^-\,(aq) \rightarrow HCO_3^-\,(aq) \tag{B}$$

$$HCO_3^-\,(aq) + OH^-\,(aq) \rightarrow H_2O + CO_3^{2-}\,(aq) \tag{C}$$

$$Ca^{2+}\,(aq) + CO_3^{2-}\,(aq) \rightarrow CaCO_3\,(s) \tag{D}$$

Several authors have studied the calcium carbonate precipitation process in relation with the kinetics of the nucleation and growth processes [6,7] using a mixture of carbon dioxide and nitrogen for the gas phase and calcium hydroxide for the liquid phase. These authors have concluded that the solid phase formed could be divided into two groups: large particles and many fine particles. This behaviour had not been corrected by means of the seeding technique.

The gas/liquid reactors (column and stirred vessels, with and without bubbling) are important and have a lot of applications in several industries (waste treatment and food processing). Gas pollutant separation processes employ a great number of this kind of equipment. For this reason, the optimization of the values of the operational variables and specifically, modeling of the gas/liquid mass transfer process evokes great interest [8,9].

In the present paper, the role of the gas/liquid mass transfer process and the connected parameters and variables in the calcium carbonate precipitation process has been analyzed.

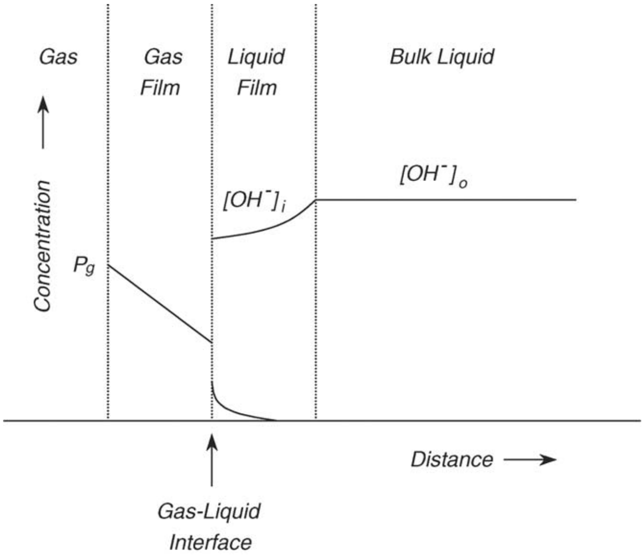

Fig. 1. Concentration profiles for a gas/liquid absorption with chemical reaction.

2. Experimental

A stirred reactor has been described previously in other papers of our group [10]. The reactor used was built in glass with an internal diameter of 11 cm, and 16 cm of height. The volume of liquid phase used was 1 L. In its internal wall, four baffles were placed in order to improve the mixing and prevent vortex formation during stirring. The gas was introduced into the reactor through the top of the vessel. The stirrer was a six-blade Rushton turbine made of metal with a diameter of 5 cm (Fig. 1).

All the experiments were carried out at 298.15 K using a thermostat shown in the experimental set-up in Fig. 2. The gas to be absorbed, pure CO_2, was passed through two humidifiers at 298.15 K and entered the contact device at a constant flowrate that was measured with a bubble flowmeter. The carbon dioxide was passed through two humidifiers to prepare the gas phase and to prevent equimolecular contra-diffusion. The gas absorption rate was calculated as the difference between inflow and outflow rates. The operation regime was semicontinuous (continuous in relation with the gas phase and batch for absorbent).

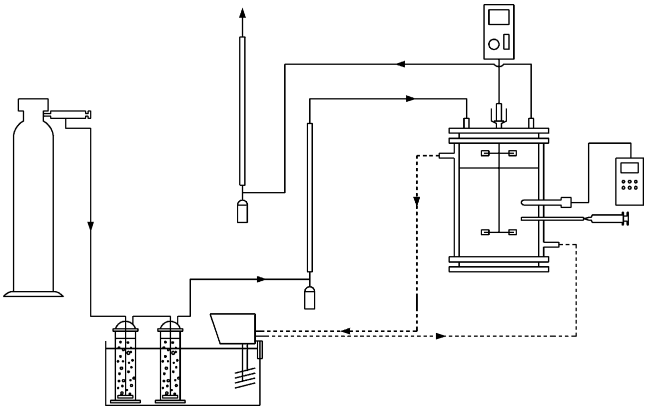

Fig. 2. Experimental set-up used in the gas/liquid mass transfer and precipitation processes.

Aqueous solutions of calcium hydroxide were prepared in the stirred vessel in an inert atmosphere to prevent the possible nucleation process by a reaction between the solute and the carbon dioxide present in the laboratory air. A carbon dioxide stream, with different values of flowrates (5–12.5 L h^{-1}), was fed to the contactor when the solution was obtained perfectly. pH of the liquid phase present in the contactor was recorded continuously. Several samples of the slurry contained in the reactive system were taken to perform the subsequent analyses. All the experiments were carried out under stirring at a rate of 350 rpm.

The pH values were obtained using a pH-meter Crison GLP 22. This pH-meter was calibrated using the two typical standards supplied by Crison (pH 4.01 and 7.00).

3. Results and discussion

In the present paper, to characterize the precipitation process accompanying the chemical reaction, the operational variables were varied in previously defined ranges. Different initial concentrations of calcium hydroxide and carbon dioxide inlet flowrates have been analyzed.

A great number of studies have analyzed the effect of different substances (additives) upon the mass transfer process. One kind of these studies is related to the effect produced by the presence of solids upon the mass transfer kinetics. When the absorption/precipitation process increases the presence of calcium carbonate in the reactor, is necessary take into account the effect of solid calcium carbonate upon the overall process. Different and opposite conclusions were obtained by several researchers regarding the effect of solid calcium carbonate present in the gas/liquid mass transfer [11–13]. For this reason, first, several experiments in relation to the effect of different particles (calcium carbonate) upon the gas/liquid mass transfer process were carried out. The experimental results obtained in this study of the volumetric mass transfer process have been presented in Fig. 3.

In this figure, it can be seen that solid particles had no effect upon the mass transfer rate. Other studies have concluded that there exists a certain influence of the solid particles upon the absorption process, but those studies are related to bubbling contactors when the effect of the solids as adsorption surfaces could favor the global gas/liquid absorption process [14,15].

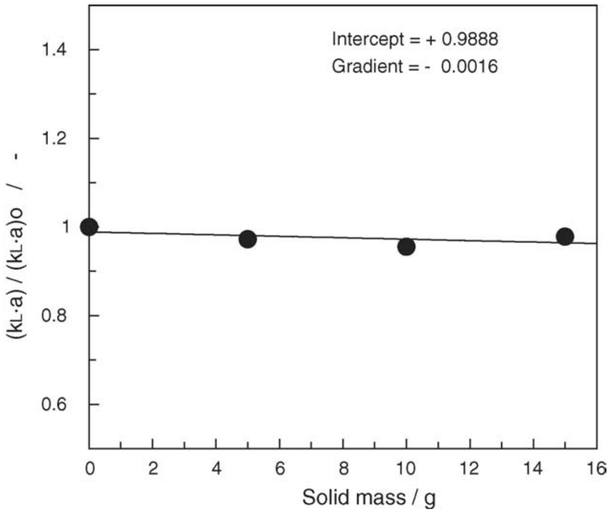

Fig. 3. Effect of solid calcium carbonate present in the liquid phase on the mass transfer process.

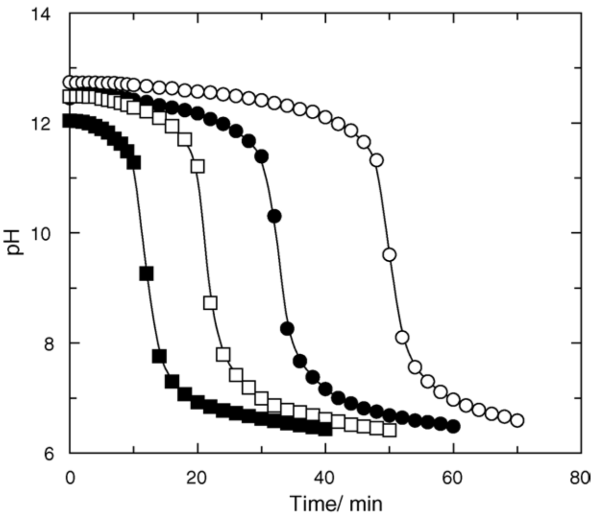

Fig. 4. Effect of calcium hydroxide initial concentration upon the pH profile: (○) $[Ca(OH)_2]_0 = 0.020$ M; (●) $[Ca(OH)_2]_0 = 0.015$ M; (☐) $[Ca(OH)_2]_0 = 0.010$ M; (■) $[Ca(OH)_2]_0 = 0.005$ M. $Q_g = 10$ L h^{-1}; stirring rate = 350 rpm.

One of the studies included in the present paper is related to the effect produced by the calcium hydroxide initial concentration upon the global absorption/precipitation process and to study this effect, this initial concentration was varied over a wide range of the solubility value in water.

Fig. 4 shows the effect of the calcium hydroxide initial concentration upon the mass transfer rate at a constant carbon dioxide inlet flowrate.

It is possible to observe that when the initial concentration of calcium hydroxide increases a delay in the pH drop corresponding to the final of the chemical reaction is produced. Since this behaviour was expected, the carbon dioxide was fed into the contact device with a constant flowrate.

A similar behaviour was observed when different experiments were carried out on a fixed calcium hydroxide initial concentration and the inlet gas flowrate to the reactor was varied. In this case, at low flowrates the final product of the reactive process is more difficult to reach. The behaviour commented is shown in Fig. 5.

The experimental data plotted in this figure allow to conclude that an increase in the carbon dioxide gas flowrate causes an increase in the speed of the global process carried out. Figs. 4 and 5 show that the global absorption/precipitation process is conditioned by the rate at which the gas (one of the reactants) is transferred to the liquid phase. For this reason, it is necessary to understand the mechanism corresponding to the absorption process in order to modelize and optimize the global process. On the basis of the contact device employed in the present paper (constant interface area), the effect of the gas flowrate must be negligible. However, it is indicated in Fig. 5 that an influence of this variable exists on the mass transfer oper-

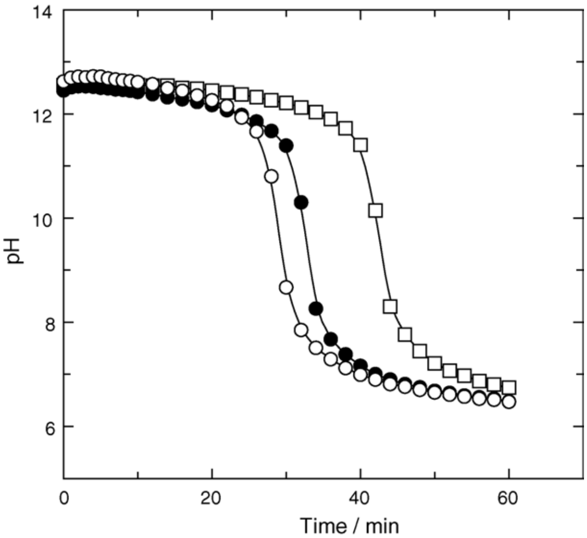

Fig. 5. Influence of gas flowrate upon the pH at different values of calcium hydroxide initial concentration: 12.5 L h^{-1} (○); 10 L h^{-1} (●); 5 L h^{-1} (□). Stirring rate = 350 rpm.

ation. This influence of the gas flowrate upon the mass transfer kinetics is due to the way of feeding the contactor with the gas; in this case, it is a direct jet on the liquid surface. It produces ripples at the mass transfer interface, with a higher effect when the gas flowrate is higher [16].

Due to the mass transfer process being the lower step of the global process, it is necessary to study the carbon dioxide transport to the liquid phase. This transport related to the fast chemical reaction was studied by Danckwerts and Sharma [17] for the reaction between carbon dioxide and hydroxyl ions. The absorption of this gas is widely affected by the presence of the OH$^-$ radical. The enhancement factor depends upon the value of the mass transfer coefficient in the absence of the chemical reaction, the hydroxyl ions' concentration, diffusivity of the reactants in the liquid phase and the values for the kinetic constants for the reactions evolved in the global process. Under certain conditions, the hydroxide concentration at gas/liquid interface could be the same as that in the liquid bulk and the reaction could be carried out completely at the interface.

$$N = C^*_{\mathrm{CO_2}} \cdot a \cdot \sqrt{D_{\mathrm{A}} \cdot k_2 \cdot C^{\mathrm{bulk}}_{\mathrm{OH^-}}} \tag{1}$$

where N is the absorption rate of carbon dioxide, $C^*_{\mathrm{CO_2}}$ and D_{A} the solubility and diffusivity of carbon dioxide in the aqueous phase, a the interface area, k_2 the rate constant for the reaction between carbon dioxide and hydroxyl ions and $C^{\mathrm{bulk}}_{\mathrm{OH^-}}$ is the OH$^-$ concentration in the bulk of aqueous phase.

The following conditions must be satisfied (Eqs. (2) and (3)):

$$\frac{\sqrt{D_{\mathrm{A}} \cdot k_2 \cdot C^{\mathrm{bulk}}_{\mathrm{OH^-}}}}{k_{\mathrm{L}}} \gg 1 \tag{2}$$

$$\frac{\sqrt{D_{\mathrm{A}} \cdot k_2 \cdot C^{\mathrm{bulk}}_{\mathrm{OH^-}}}}{k_{\mathrm{L}}} \ll \frac{C^{\mathrm{bulk}}_{\mathrm{OH^-}}}{z \cdot C^*_{\mathrm{CO_2}}} \cdot \sqrt{\frac{D_{\mathrm{B}}}{D_{\mathrm{A}}}} \tag{3}$$

where k_{L} is the liquid side mass transfer coefficient in the absence of chemical reaction, z the stoichiometric coefficient of the overall reaction ($z = 2$) and D_{B} is the diffusivity of OH$^-$ ions in the liquid phase.

If the condition presented in Eq. (2) is not satisfied, it implies that a part of the chemical reaction between carbon dioxide and hydroxyl ions is carried out at the interface and the other part in the bulk of the liquid. The surface renewal theory developed by Dankwerts contributed to the expression shown in Eq. (4):

$$N = C^*_{\mathrm{CO_2}} \cdot a \cdot \sqrt{D_{\mathrm{A}} \cdot k_2 \cdot C^{\mathrm{bulk}}_{\mathrm{OH^-}} + k_{\mathrm{L}}^2} \tag{4}$$

When the studied system implies absorption due to a chemical reaction of carbon dioxide into the electrolyte solution, it is necessary to take into account the effect of this reaction into the gas solubility value. The value of gas solubility could be calculated using the equation (Eq. (5)) developed by Setschenow [18] and modified by van Krevelen and Hoftijzer [19]:

$$\log\left(\frac{C^{*,\mathrm{solution}}_{\mathrm{CO_2}}}{C^{*,\mathrm{water}}_{\mathrm{CO_2}}}\right) = -K_{\mathrm{S}} \cdot I \tag{5}$$

where K_{S} is the salting-out parameter and I is the ionic strength.

The enhancement parameter is defined as the sum of the contributions of all ions present in the solution and the carbon dioxide absorbed in the liquid phase (Eq. (6)).

$$K_{\mathrm{S}} = i_- + i_+ + i_{\mathrm{g}} \tag{6}$$

Several authors have employed these expressions with some modifications. Hikita et al. [20] and Vázquez et al. [21] used these equations to determine the solubility of gases in electrolyte solutions, but they employed the product of the salting-out parameter and ionic strength for each compound using the expression developed by Danckwerts and Gillham [22],

$$K_{\mathrm{S}} \cdot I = \sum_i K_{\mathrm{S}_i} \cdot I_i = K_{\mathrm{S}_1} \cdot I_1 + K_{\mathrm{S}_2} \cdot I_2 + K_{\mathrm{S}_3} \cdot I_3 + \cdots \tag{7}$$

where K_{S_1}, K_{S_2}, K_{S_3} are the salting-out parameters corresponding to the compounds presents in the system and I_i is its corresponding ionic strength.

On the other hand, Onda et al. [23] developed an expression to calculate the salting-out parameter directly as the sum of contributions from all ions and gases present in gas/liquid system. The final expression is shown in Eq. (8) employing the global ionic strength of solution:

$$\frac{C^{*,\mathrm{solution}}_{\mathrm{CO_2}}}{C^{*,\mathrm{water}}_{\mathrm{CO_2}}} = 10^{-(i_- + i_+ + i_{\mathrm{g}}) \cdot I} \tag{8}$$

In present paper, the equation developed by Onda et al. will be used to calculate the salting-out parameter to apply the equation modified by van Krevelen and Hoftijzer. The values corresponding to the i parameter have been obtained from bibliography [18] and the values for the Ca^{2+}, OH$^-$ ions and carbon dioxide were −0.0547, 0.3875 and 0.2277, respectively.

Using the values obtained for the parameter I, it is possible to calculate the value corresponding to the enhancement factor (K_{s}) for the system employed in the present paper. And then, using

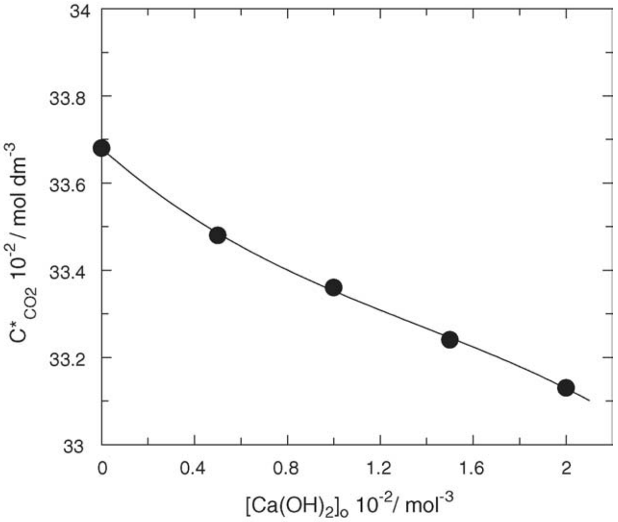

Fig. 6. Effect of calcium hydroxide on the carbon dioxide solubility.

Eq. (5) the solubility of carbon dioxide in aqueous solutions of calcium hydroxide was calculated. In Fig. 6, the effect of the electrolyte concentration upon the carbon dioxide solubility is shown. The calculated values for gas solubility indicate that the presence of electrolyte produces a decrease in the solubility value. Carbon dioxide solubility value in pure water has been obtained from data collected by Linke [24].

In the chemical reactions that involve a previous transfer of one reagent from gas to liquid phase, it is necessary to take into account that the gas is absorbed previously and a part of this gas reacts with the other reagent and the other part remains absorbed. The quantities of each part depend on the kinetics of the chemical reaction. In the present work, the reaction is very fast and practically all the carbon dioxide absorbed reacts instantaneously.

With the experimental values of the recorded pH and the carbon dioxide absorbed and using a speciation program as used by other researchers [23], it was possible to know the concentration of each species present in the reactor. This calculus allows to determine the quantity of carbon dioxide that remains absorbed.

In relation with the conditions shown in Eqs. (2) and (3), it must be taken into account that the experimental data for absorption is divided into two zones. The first one satisfied Eq. (2) and then Eq. (1) could be applied to fit the absorption data to calculate the value for the gas/liquid mass transfer area.

On the other hand, if the condition shown in Eq. (2) is not satisfied, the experimental data were used to calculate the value of the liquid side mass transfer coefficient based on the surface renewal theory of Danckwerts.

To analyze the absorption/precipitation global process, the initial concentration of calcium hydroxide and the feed gas flowrate were varied. Fig. 8 shows the values corresponding to the interchange area and liquid side individual mass transfer coefficient calculated using the experimental absorption data. On the basis of these values, it is possible to observe that in both cases (for area and mass transfer coefficient) the gas flowrate does not have any effect on the value of these two parameters.

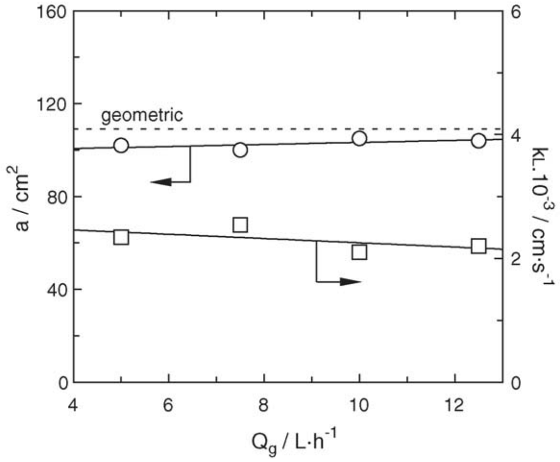

Fig. 7. Effect of gas flowrate upon the value of the liquid side mass transfer coefficient and area $[Ca(OH)_2]_0 = 0.015$ M; stirring rate = 350 rpm.

Compared with the observed effect produced by the gas flowrate on the mass transfer coefficient, similar behaviours were observed in other systems by different authors.

The effect of initial calcium hydroxide concentration upon the carbon dioxide solubility has been commented previously (Fig. 6). The experiments shown in Fig. 7 have been carried out at a constant value of calcium hydroxide initial concentration ($[Ca(OH)_2]_0 = 0.015$ M) and then the solubility of carbon dioxide in the liquid phase was found to be constant.

Also, no effect was observed upon the interfacial area due to the gas flowrate. In this kind of reactor, the effect of the gas flowrate is negligible compared to the effect produced by this operational variable in bubble reactors (tanks and columns). In Fig. 7, the value of the mass transfer area calculated through the geometric characteristics of the contact device has been plotted. All the values calculated using the absorption experiments have a minor value of the “geometric” area. This behaviour is due to the system studied in the present paper in which a chemical reaction is produced in the liquid phase, and this reaction is very fast, the chemical reaction is produced totally in the proximity of the gas/liquid interface. The reaction employed in this work concludes with a solid formation. Because the reaction is produced at the interface in a high grade, the solid phase is formed in the interface and then the solid remains in the liquid surface for a certain period of time until is sent to the bulk of the liquid phase by the effect of the stirring rate.

The presence of the solid phase produced at the interface invokes a decrease in the effective mass transport area, and this effect is observed in the values of area determined experimentally.

Experimental results of the effect of calcium hydroxide initial concentration upon the commented parameters related to the gas/liquid mass transfer process for the area and the individual mass transfer coefficient are shown in Fig. 7. A different behaviour has been observed in this case compared to the previous figure: a notable effect upon the absorption parameters has been observed.

In the case of the mass interchange area, a clear trend is observed due to the presence of calcium hydroxide in the liquid

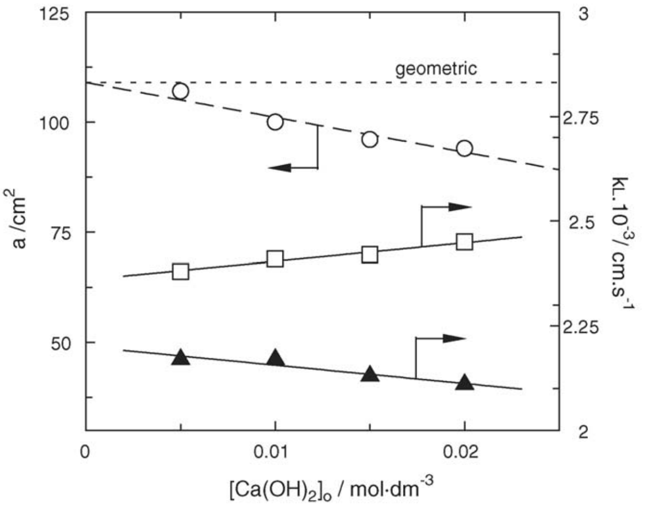

Fig. 8. Effect of calcium hydroxide initial concentration upon the value of the liquid side mass transfer coefficient and area. $Q_g = 10\,\mathrm{L\,h^{-1}}$; stirring rate = 350 rpm. (◯) Interfacial area, (☐) mass transfer coefficients and (▲) mass transfer coefficient without chemical reaction.

phase. The solute concentration implies a decrease in the value of the effective area. This behaviour is explained on the basis of the theories developed previously in relation to the decrease in the mass transfer effective area due to the solid phase formation at the interface. When the calcium hydroxide concentration increases in the liquid phase, it also increases in the liquid film at the interface and then the frequency of solid formation increases and produces a higher occupation of the interface than a minor calcium hydroxide initial concentration.

The last point is related to the effect of the presence of a reagent in the liquid phase on the individual liquid side mass transfer coefficient values. The calcium hydroxide concentration invokes a continuous increase in the value of the mass transfer coefficient. This increase is explained on the basis of the effect produced by the increase in driving force in relation with the nonreactive system. In Fig. 8, the observed trend was plotted. Nonreactive systems produce a slight decrease on mass transfer coefficient when solute concentration increases due to the decrease in carbon dioxide solubility (related also with driving force value).

For the solid phase obtained by the precipitation process in the stirred reactor, observed during the gas/liquid absorption process, it was commented above that samples of 5 mL of the slurry were created in the contact device. These samples were analyzed using different techniques. Also, when the absorption/precipitation reaction process was completed, the slurry created in the reactor was filtered using a 0.22 μm pore size filter. The samples and the final precipitate were analyzed by IR spectroscopy to determine the nature of the solid phase created. Also, SEM photographs were taken to determine the shape of the solid phase, and with this data the type of solid produced can be determined.

The IR spectra obtained for the solid phase formed by the chemical reaction between carbon dioxide and calcium hydroxide indicate that the solid was in all cases calcium carbonate as confirmed in the literature [25]. An example of the IR spectra obtained is shown in Fig. 9, with a characteristic band at ≈1425 $\mathrm{cm^{-1}}$.

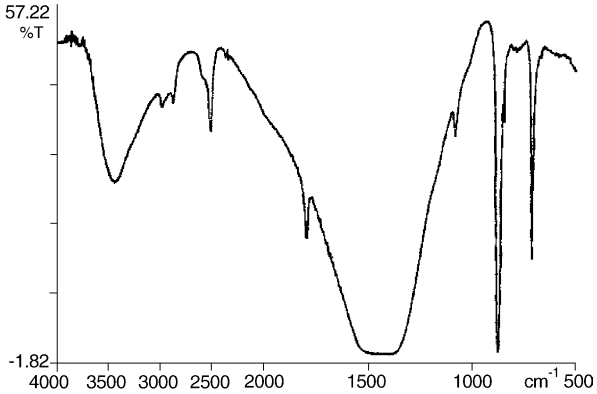

Fig. 9. IR spectrum corresponding to a solid sample obtained from the slurry filtration.

Since the calcium carbonate can exist at different polymorphs (calcite, aragonite, vaterite) [26], it was necessary to analyze the shape of the solid (calcium carbonate) produced in the gas/liquid system to determine the polymorphs present.

Fig. 10 is an example of the SEM micrographs obtained for the solid samples taken at the end of the absorption/precipitation process. The photographs allow to obtain two conclusions. (i)

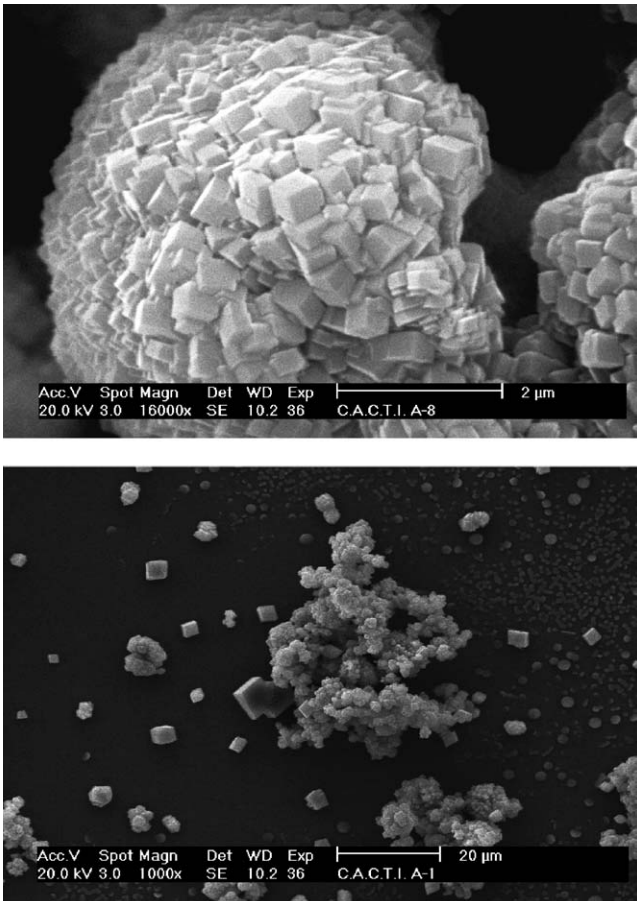

Fig. 10. Electron microscopy photograph of the solid phase formed in the gas/liquid reactor.

The shape of the solid crystals was cubic in all cases analyzed. This shape is characteristic of the calcite polymorph and based on the SEM taken of the solid samples, the solid formed in the system employed in the present paper was calcite in all cases. (ii) The other conclusion is that the aggregation phenomena observed in Fig. 10 are very interesting and are affected significantly by the particle size distribution because the aggregates reach a large size due to the great number of individual crystals that form the aggregate.

The high level observed in the aggregation phenomena, similar to the results obtained by other authors [27], is due to the high supersaturation reach in the liquid film near the gas/liquid interface. At the liquid film, the carbon dioxide absorbed is accumulated and it creates a high concentration compared to the bulk liquid. Due to the fast reaction that occurs at the liquid phase, carbon dioxide reacts and produces the solid phase quickly and the probability of collision of the individual crystals is very high and leads to the aggregation of the calcite crystals.

Acknowledgement

The authors thank the regional government of Galicia (Xunta de Galicia) for financial support of their work (PGIDIT03-TAM20902PR).

References

[1] S.J. Yoon, H. Lee, J.-H. Yoon, J.-G. Shim, J.-K. Lee, B.-Y. Min, H.-M. Eum, Kinetics of absorption of carbon dioxide into aqueous 2-amino-2-ethyl-1,3-propanediol solutions, Ind. Eng. Chem. Res. 41 (2002) 3651–3656.

[2] K. Uebo, R. Yamazaki, K. Yoshida, Precipitation mechanism of calcium carbonate fine particles in a three-phase reactor, Adv. Powder Technol. 3 (1992) 71–79.

[3] J. García-Carmona, J. Gómez-Morales, R. Rodríguez-Clemente, Rhombohedral–scalenohedral calcite transition produced by adjusting the solution electrical conductivity in the system $Ca(OH)_2$–CO_2–H_2O, J. Colloids Interface Sci. 261 (2003) 434–440.

[4] S. Wachi, A.G. Jones, Effect of gas–liquid mass transfer on crystal size distribution during the batch precipitation of calcium carbonate, Chem. Eng. Sci. 46 (1991) 3289–3293.

[5] H. Hikita, S. Asai, T. Takatsuka, Absorption of carbon dioxide into aqueous sodium hydroxide and sodium carbonate–bicarbonate solutions, Chem. Eng. J. 11 (1976) 131–141.

[6] Y. Kotaki, H. Tsuge, Reactive crystallization of calcium carbonate in a batch crystallizer, J. Cryst. Growth 99 (1990) 1092–1097.

[7] H. Yagi, S. Nagashima, H. Hikita, Semibatch precipitation accompanying gas–liquid reaction, Chem. Eng. Commun. 65 (1988) 109–119.

[8] E. Álvarez, B. Sanjurjo, A. Cancela, J.M. Navaza, Mass transfer and influence of physical properties of solutions in a bubble column, Chem. Eng. Res. Des. 78 (2000) 889–893.

[9] G. Vázquez, M.A. Cancela, R. Varela, E. Álvarez, J.M. Navaza, Influence of surfactants on absorption of CO2 in a stirred tank with and without bubbling, Chem. Eng. J. 67 (1997) 131–137.

[10] D. Gómez-Díaz, J.M. Navaza, Effect of ethylene glycol on the CO2/water gas–liquid mass transfer process, Chem. Eng. Technol. 26 (2002) 75–80.

[11] M.V. Dagaonkar, A.A.C.M. Beenackers, V.G. Pangarkar, Enhancement of gas–liquid mass transfer by small reactive particles at realistically high mass transfer coefficients: absorption of sulfur dioxide into aqueous slurries of $Ca(OH)_2$ and $Mg(OH)_2$ particles, Chem. Eng. J. 81 (2001) 203–212.

[12] O. Ozkan, A. Calimli, R. Berber, H. Oguz, Effect of inert solid particles at low concentrations on gas–liquid mass transfer in mechanically agitated reactors, Chem. Eng. Sci. 55 (2000) 2737–2740.

[13] M. Tobajas, E. Garcia-Calvo, M.H. Siegel, S.E. Apitz, Hydrodynamics and mass transfer prediction in a three-phase airlift reactor for marine sediment biotreatment, Chem. Eng. Sci. 54 (1999) 5347–5354.

[14] S.Y. Park, W.S. Choi, Effects of operating factors on the particle size distribution and particle shape of synthesized precipitated $CaCO_3$: effect of reaction temperature, blowing rate of CO_2 gas and initial slurry concentration of $Ca(OH)_2$ on reaction completion time, Adv. Powder Technol. 15 (2004) 1–12.

[15] E. Sada, H. Kumazawa, C.H. Lee, Chemical absorption in a bubble column loading concentrated slurry, Chem. Eng. Sci. 38 (1983) 2047–2051.

[16] D. Gómez-Díaz, J.M. Navaza, Gas/liquid mass transfer processes in a carbon dioxide/alkane system, J. Chem. Technol. Biotechnol. 80 (2005) 812–818.

[17] P.V. Danckwerts, M.M. Sharma, Absorption of carbon dioxide into solutions of alkalies and amines. Hydrogen sulfide and carbonyl sulfide, Chem. Eng. Lond. 202 (1966) CE244–CE280.

[18] K. Onda, E. Sada, T. Kobayashi, S. Kito, K. Ito, Salting-out parameters of gas solubility in aqueous salt solutions, J. Chem. Eng. Japan 3 (1970) 18–24.

[19] D.W. van Krevelen, P.J. Hoftijzer, Kinetics of simultaneous absorption and chemical reaction, Chem. Eng. Progr. 44 (1948) 529–536.

[20] H. Hikita, S. Asai, H. Ishikawa, N. Esaka, Solubility of nitrous oxide in sodium carbonate-sodium bicarbonate solutions at 25 °C and 1 atm, J. Chem. Eng. Data 19 (1974) 89–92.

[21] G. Vázquez, M.A. Cancela, C. Riverol, E. Álvarez, J.M. Navaza, Determination of interfacial areas in a bubble column by different chemical methods, Ind. Eng. Chem. Res. 39 (2000) 2541–2547.

[22] P.V. Danckwerts, A.J. Gillham, The design of gas absorbers. I. Methods for predicting rates of absorption with chemical reaction in packed columns, and tests with 1 1/2-inch Raschig rings, Trans. Inst. Chem. Eng. 44 (1966) T42–T54.

[23] J. Gómez-Morales, J. Torrent-Burgués, R. Rodríguez-Clemente, Nucleation of calcium carbonate at different initial pH conditions, J. Cryst. Growth 169 (1996) 331–338.

[24] W.F. Linke, Solubilities, vol. II, fourth ed., American Chemical Society, Washington, DC, 1965.

[25] C.Y. Tai, P.-C. Chen, S.-M. Shih, Size-dependent growth and contact nucleation of calcite crystals, AIChE J. 39 (1993) 1472–1482.

[26] L. Xiang, Y. Xiang, Z.G. Wang, Y. Jin, Influence of chemical additives on the formation of super-fine calcium carbonate, Powder Technol. 123 (2002) 129–133.

[27] Y. Kotaki, H. Tsuge, Reactive crystallization of calcium carbonate by gas–liquid and liquid–liquid reactions, Can. J. Chem. Eng. 68 (1990) 435–442.