

Article

# CO<sub>2</sub> Capture in A Bubble-Column Scrubber Using MEA/CaCl<sub>2</sub>/H<sub>2</sub>O Solution—Absorption and Precipitation

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Received: 15 June 2020; Accepted: 7 August 2020; Published: 11 August 2020



**Abstract:** This study used the solvent monoethylamine (MEA)/CaCl<sub>2</sub>/H<sub>2</sub>O to investigate CO<sub>2</sub> absorption and CaCO<sub>3</sub> crystallization in a bubble column scrubber. The variables explored were pH, gas flow rate, gas concentration, the liquid flow rate of the solution to absorb CO<sub>2</sub>, and CaCO<sub>3</sub> crystallization. Under a continuous mode, the solution of CaCl<sub>2</sub> was fed continuously, and the pH dropped after CO<sub>2</sub> absorption. To maintain the set pH value, there was an automatic input of the MEA solvent into the bubble column. In addition to maintaining the pH, the solution could also absorb CO<sub>2</sub> and produce CaCO<sub>3</sub> crystals, which served two purposes. The results showed that there were mainly vaterite crystals. At different pH values, the lower the pH, the higher the precipitation rate of vaterite ( $F_p$ ), and vice versa. However, under different gas flow rates, the  $F_p$  decreased as the pH value increased. Additionally, the process variables also affected the absorption rate ( $R_A$ ) and the overall mass-transfer coefficient ( $K_{GA}$ ) generally increased with increasing pH, gas concentration, and gas flow rate. However, it slowed down under operating conditions at high pH and high gas flow rate. Finally, correlation equations for  $R_A$ ,  $K_{GA}$ , and  $F_p$  were also obtained and discussed in the study.

**Keywords:** absorption; precipitation; bubble column scrubber

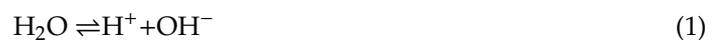
## 1. Introduction

The weather irregularity resulting from the greenhouse effect is a matter of great concern around the world. A major portion of greenhouse gases is CO<sub>2</sub>, which is mainly caused by the excessive use of fossil fuels and unchecked deforestation [1,2]. Many countries are working towards alternative energy development [3], energy-saving, and process improvement. Chemical treatment, physical treatment, and microbiological treatment are the primary technologies for disposing of the CO<sub>2</sub> emitted from factories, and the most commonly used method used is chemical treatment [4,5]. More than 1000 factories have developed the alkanolamine processes over the past few decades, among which the monoethylamine (MEA) process has the advantages in terms of price, characteristics, and recovery, although, it still consumes energy during recovery and brings cost burdens due to the treatment of concentrated CO<sub>2</sub> [5]. To develop an energy-saving process, new solvents [6–10], and new processes [11,12] have been proposed and explored to find a process with a lower regeneration energy requirement. Some of them studied the absorption kinetics of the mixed solvents [9,13,14]. Alternatively, the hot potassium carbonate process is also applied in many cases, however, solvent regeneration and reuse during recovery not only increases the cost but also causes secondary pollution [1,15]. The issue with the NaOH process is that the solvent cannot be recovered. For the processes focusing on resource recycling, the hot potassium carbonate and the NaOH processes are less effective. Hence, this research team has developed the Ca(OH)<sub>2</sub> process for CO<sub>2</sub> absorption, which can recover CO<sub>2</sub> and produce

CaCO<sub>3</sub> without solvent recovery. However, due to the inability of continuous operation, the process development was limited. Eventually, the process was changed, and BaCl<sub>2</sub>/NaOH/H<sub>2</sub>O was used for CO<sub>2</sub> absorption, which could produce BaCO<sub>3</sub> and be operated continuously [16,17]. However, limitations still exist in solvent reuse. Previous studies showed that the CO<sub>2</sub> absorption rate is greatly affected by pH because while an increase in pH improves the CO<sub>2</sub> removal efficiency, it consumes more NaOH, which raises the cost. In addition, an increase in the liquid flow rate improves the yield of BaCO<sub>3</sub>, and an increase in the gas flow rate improves the CO<sub>2</sub> removal efficiency.

To develop CO<sub>2</sub> and for resource recycling, this team also tried to recover CO<sub>2</sub> and produce CaCO<sub>3</sub> by MEA/CaCl<sub>2</sub>/H<sub>2</sub>O, and tested solvent reuse. The results showed that the recovered solvent can also absorb CO<sub>2</sub>, which motivated us to develop this process. Hence, because of the advantage of the bubble column, with MEA/CaCl<sub>2</sub>/H<sub>2</sub>O as the solvent, CO<sub>2</sub> recovery and resource recycling were carried out by continuously operating a bubble column [18–21].

The main equations for the reaction with MEA/CaCl<sub>2</sub>/H<sub>2</sub>O as the solvent are as follows [8,22]:



Equations (1), (4) and (5) present the change in the hydrolysis of the carbonate ion, and Equations (6), (7) present the reaction of using MEA solution for CO<sub>2</sub> absorption. RNCOO<sup>−</sup>(aq) is hydrolyzed into HCO<sub>3</sub><sup>−</sup> and RNH<sub>2</sub> after production and then reacts with Ca<sup>2+</sup> to precipitate CaCO<sub>3</sub> because HCO<sub>3</sub><sup>−</sup> can be further dissociated to CO<sub>3</sub><sup>2−</sup>. MEA exhibits excellent absorption efficiency, therefore, it has been adopted in several studies.

In the previous studies, to understand the relationship between absorption and crystallization in this system, the quasi-steady operation and shell balance were adopted to obtain the equation of absorption rate, and a two-film model was used to describe the mass transfer of CO<sub>2</sub> in the absorption solvent to determine the overall mass transfer coefficient [16,23]. Hence, the results of this study were compared with those of the previous studies in terms of the above-mentioned theory to understand the commercial value of this process. Further, the yield of the recovered solid was determined by the liquid flow rate and suspension concentration, and the relationship between absorption rate and precipitation rate was used to obtain the design parameters of the absorber.

As a result, with MEA/CaCl<sub>2</sub>/H<sub>2</sub>O as the absorbent, MEA as the controller of the pH of the system, CaCl<sub>2</sub> as the precipitant, and pH value, CO<sub>2</sub> concentration and CO<sub>2</sub> flow rate as the variables, this study aimed to investigate the effects of variables on the absorption rate, mass transfer coefficient, and precipitation rate by CO<sub>2</sub> absorption experiment in the bubble column, so as to provide references for the design of such absorbers.

## 2. Absorption Rate and Mass Transfer Coefficient

The gases A (CO<sub>2</sub>) and B (N<sub>2</sub>) were mixed and added to the bubble column, and the calcium chloride aqueous solution and MEA solvent were separately imported into the bubble column. At the

beginning of the experiment, the calcium chloride solution was continuously fed at 50 mL/min and the MEA was fed to adjust the decline of pH value due to CO<sub>2</sub> absorption to keep it within the set range. MEA balanced pH value and absorbed the CO<sub>2</sub>. The absorbed CO<sub>2</sub> decomposed to CO<sub>3</sub><sup>2-</sup> in the solution and quickly reacted with Ca<sup>2+</sup> in the solution to form CaCO<sub>3</sub> precipitation. CO<sub>2</sub> was continuously fed and MEA was fed to maintain absorption, finally, the CO<sub>2</sub> at the outlet was steady, indicating that the system was now stable. The mass balance at a steady state of CO<sub>2</sub> is shown below [16]:

$$F_{A1} - F_{A2} - R_A V_L = 0 \quad (10)$$

where,  $F_{A1}$  and  $F_{A2}$ , respectively, denote the molar flow rates at the CO<sub>2</sub> inlet and outlet,  $V_L$  represents the liquid volume in the bubble column and  $R_A$  represents the CO<sub>2</sub> absorption rate, which can be obtained by the following equation:

$$R_A = \frac{F_{A1}}{V_L} \left[ 1 - \left( \frac{1 - y_1}{y_1} \right) \left( \frac{y_2}{1 - y_2} \right) \right] \quad (11)$$

where,  $y_1$  and  $y_2$ , respectively, denote the CO<sub>2</sub> concentrations at the inlet and outlet. Once the absorption rate is obtained, the overall mass transfer coefficient can be obtained by the following equation:

$$K_G a = \frac{R_A}{[C_g - HC_L]_{av}} \quad (12)$$

where,  $H$  is Henry's law constant and a function of temperature and ionic strength. In Equation (12), because of the change in the position of the gas as it passes through the bubble column,  $C_g - HC_L$  is substituted by the average value of the inlet and outlet, thus, the calculated overall mass transfer coefficient is the average value [23]. However,  $H$ -value was found to be 0.39–0.78 [24] and CO<sub>2</sub> in the liquid phase was less than 10<sup>-6</sup> M. Due to this, the value  $HC_L$  was less than 10<sup>-6</sup> [25], which was much smaller than  $C_g$ . Therefore, the  $HC_L$  value can be negligible compared to  $C_g$ .

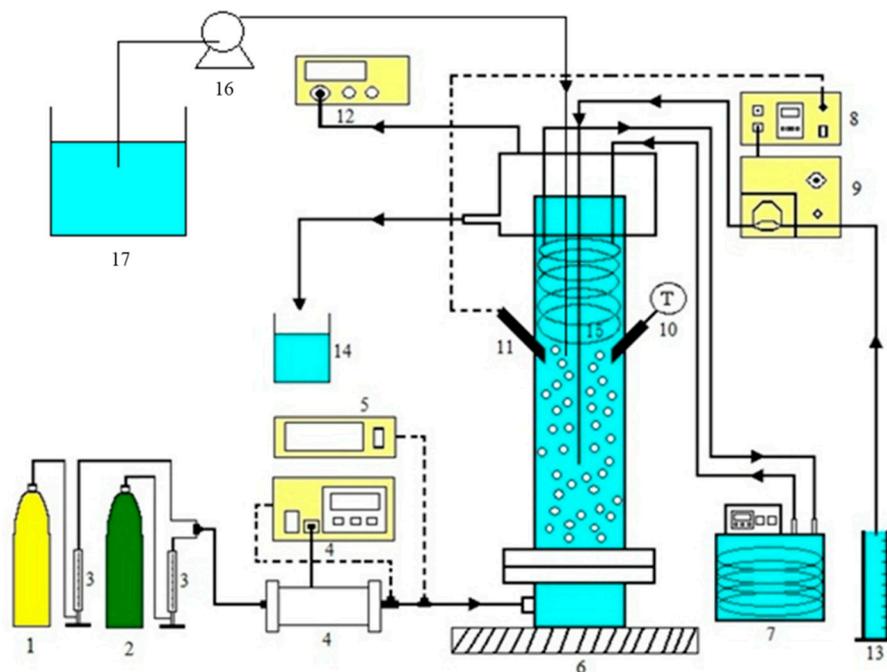
### 3. Experiment

The major equipment used in this experiment is shown in Figure 1, including the bubble column, digital pressure indicator, heater, CO<sub>2</sub> meter, condenser, pH controller, gas mixer, N<sub>2</sub> cylinder, CO<sub>2</sub> cylinder, and gas flow-meter. The reagents used in this experiment are calcium chloride, MEA, CO<sub>2</sub>, and N<sub>2</sub> gas.

Before the experiment, the pH electrode was calibrated with a standard buffer solution of pH 4.0 and 7.0 to accurately observe the change in pH. CO<sub>2</sub> and N<sub>2</sub> cylinders were opened to adjust the flow of CO<sub>2</sub> and N<sub>2</sub> and the gas temperature at the inlet until the CO<sub>2</sub> concentration and temperature of the gas mixer reached the set values. During the experiment, the prepared solution was added into the bubble column, and the gas in the gas mixer was introduced into the solution in the bubble column. To begin the operation, the condenser was opened and the calcium chloride solution was continuously fed at 50 mL/min and the MEA was fed to adjust the decline of pH after absorption to keep it within the set range. On the other hand, CO<sub>2</sub> could be absorbed. The time, pH value, the test value of the CO<sub>2</sub> meter, and MEA feeding volume were recorded during the experiment, and about 5 mL of suspension was extracted in a fixed time. After the suspension was filtered, two additional 5 mL samples of the suspension were taken at 40 and 50 min to measure the calcium ion concentration and total carbonate ion concentration by atomic absorption (AA) (GBC Scientific Equipment, GBC 932 Plus, Melbourne, Australia) At the end of the experiment, an additional 2 mL of suspension was taken and placed in a container used for particle size measurement to measure the size of CaCO<sub>3</sub> particles by using a laser particle size analyzer (Galai CIS-50, Or Akiva, Isreal).

After the experiment, the suspension reacted in the bubble column was filtered, and the obtained solid was dried using a hot air drier. Finally, the obtained powder was weighed, and part of it was observed by a SEM (Jeol, JSM-6500F, Tokyo, Japan) for its morphology, while the other part was

observed by XRD(Rigaku, D/MAX-2200/PC, Tokyo, Japan) components and construction. Table 1 shows the operating conditions of the experiment, with the CO<sub>2</sub> concentration between 10 and 30%, the gas flow rate between 2 and 8 L/min, and the pH value between 9 and 11. Table 1 was the operating conditions conducted in this study.



**Figure 1.** The capture of CO<sub>2</sub> using a bubble-column scrubber. 1. CO<sub>2</sub> gas tank; 2. N<sub>2</sub> gas tank; 3. gas-flow meter; 4. gas-flow meter; 5. digital pressure gauge; 6. bubble-column scrubber; 7. cooling machine; 8. tubing pump; 9. controller; 10. thermometer; 11. pH-electrode; 12. CO<sub>2</sub> meter; 13. MEA solvent reservoir; 14. reservoir; 15. cooling coil; 16. tubing pump; 17. CaCl<sub>2</sub> solution reservoir.

**Table 1.** Operating conditions used in this work.

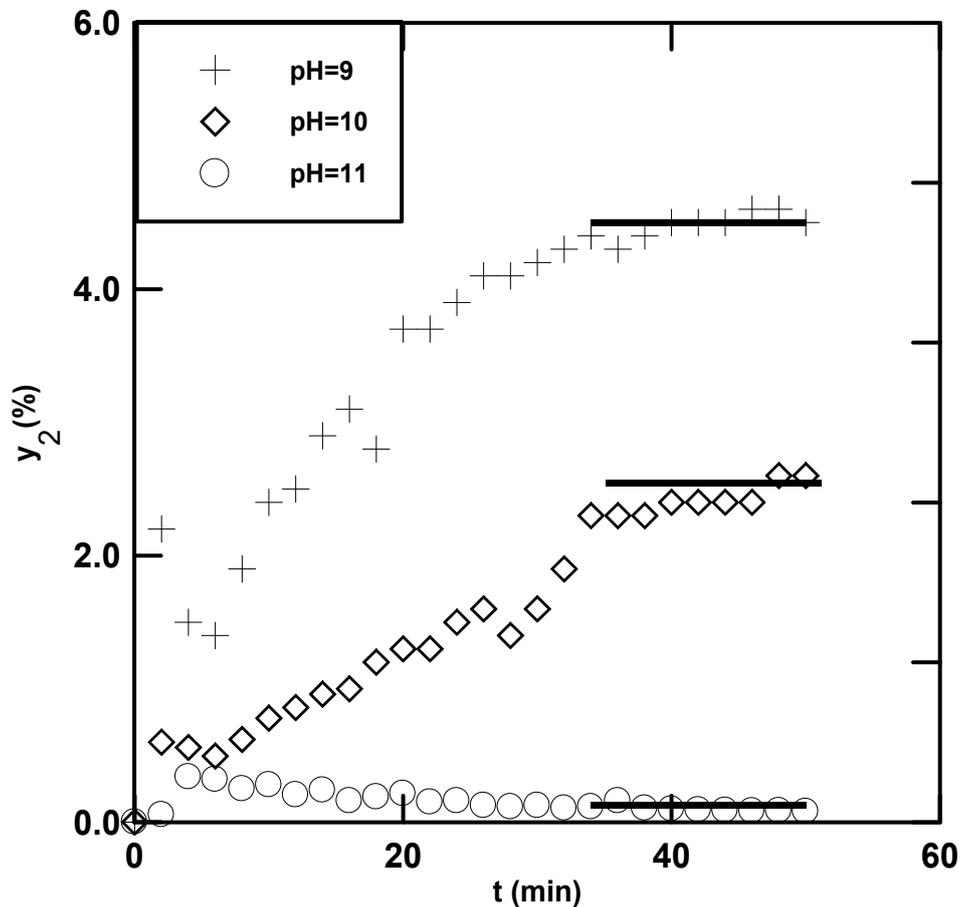
Concentration of CO <sub>2</sub> Gas (%)	10–30
Concentration of CaCl <sub>2</sub> (M)	0.2
Concentration of MEA (M)	4
Gas-flow rate (L/min)	2–8
Flow rate of CaCl <sub>2</sub> (mL/min)	50
Gas inlet temperature (°C)	30
Temperature in the column (°C)	35
pH	9–11

## 4. Results and Discussions

### 4.1. Experimental Data

Figure 2 shows the CO<sub>2</sub> concentrations at the outlet measured at  $Q_g = 4$  L/min and different pH values, indicating that, at pH 9 and 10, the CO<sub>2</sub> concentration at the outlet declined in the initial stage of the experiment, then began to rise nearly 5 min later, and reached a steady state at nearly 40 min and 34 min, respectively. At pH 11, the CO<sub>2</sub> concentration at the outlet first rose and then began to decline nearly 2 min later until it reached a steady state at about 20 min. After the steady state was reached, the absorption rate, mass transfer coefficient, mean residence time, and precipitation rate could be obtained by Equations (10) and (11), by which the precipitation rate was calculated by multiplying the slurry density by the liquid flow-rate and dividing the result by the liquid volume; the mean particle size was measured by the particle size analyzer. As shown in Table 2, the obtained absorption

rate was between  $6.26 \times 10^{-6}$  and  $3.80 \times 10^{-4}$  mol/s·L, the mass transfer coefficient was in the range between  $1.83 \times 10^{-3}$  and  $5.33 \times 10^{-2}$  1/s, the precipitation rate is was in the range of  $0.53 \times 10^{-5}$  to  $26.08 \times 10^{-5}$  mol/s·L, and the particle size was in the range of 0.72 to 1.83  $\mu\text{m}$ . Further, the absorption efficiency was found to be in the range of 32.8–100%.



**Figure 2.** Variation in  $\text{CO}_2$  concentration at the outlet with time at different pH values. ( $\text{CO}_2 = 10\%$ ,  $Q_g = 4$  L/min).

**Table 2.** The data obtained in the experiment.

No.	pH	$y_1$ (%)	$u$ (cm/s)	$R_A \times 10^5$ (mol/s·L)	$K_G a \times 10^2$ 1/s	$\tau$ min	$F_p \times 10^5$ (mol/s·L)	$E$ (%)	$d_p$ $\mu\text{m}$	$Q_{\text{add}}$ (mL/min)
1	9	10	1.7	0.63	0.183	17.00	3.42	32.8	1.60	2.0
2	10	10	1.7	1.28	0.487	16.71	1.35	71.5	1.37	2.9
3	11	10	1.7	1.82	0.889	16.01	0.53	100	1.45	2.6
4	9	10	3.4	2.40	1.38	14.98	14.71	55	1.33	9.0
5	10	10	3.4	3.07	1.54	13.92	6.11	75	1.41	13.5
6	11	10	3.4	3.88	2.66	13.56	1.34	99.2	1.83	15.2
7	9	10	5.1	5.02	1.59	9.57	11.59	68	1.14	12.4
8	10	10	5.1	7.36	4.26	9.51	2.85	100	0.64	25.3
9	11	10	5.1	7.40	4.10	4.57	1.06	100	1.78	176.6
10	9	10	6.8	9.78	3.74	11.88	13.76	84.1	1.01	20.2
11	10	10	6.8	14.4	4.31	7.70	10.68	100	0.94	44.3
12	11	10	6.8	11.5	5.20	4.95	3.08	100	1.28	228.4
13	9	20	3.4	12.3	1.53	14.17	26.08	68.7	1.63	42.4
14	10	20	3.4	16.3	2.70	11.74	9.77	97.5	1.44	43.0
15	11	20	3.4	16.4	3.03	3.90	5.43	100	0.72	143.6
16	9	30	3.4	30.8	2.99	12.60	22.50	73.4	1.65	24.4
17	10	30	3.4	38.0	5.33	9.37	10.30	98.3	1.31	64.8
18	11	30	3.4	36.9	4.76	3.18	1.68	100	0.75	128.6

#### 4.2. Identification of Solid Components

The XRD analysis (Figure 3) shows the comparison with the standard  $\text{CaCO}_3$  peak, and the results shows that the major peak intensities, (110), (112), (114), (300), (118), and position of the sample obtained from the experiment were consistent with those of the vaterites as reported earlier [26–28], indicating that the obtained  $\text{CaCO}_3$  was mainly vaterite.

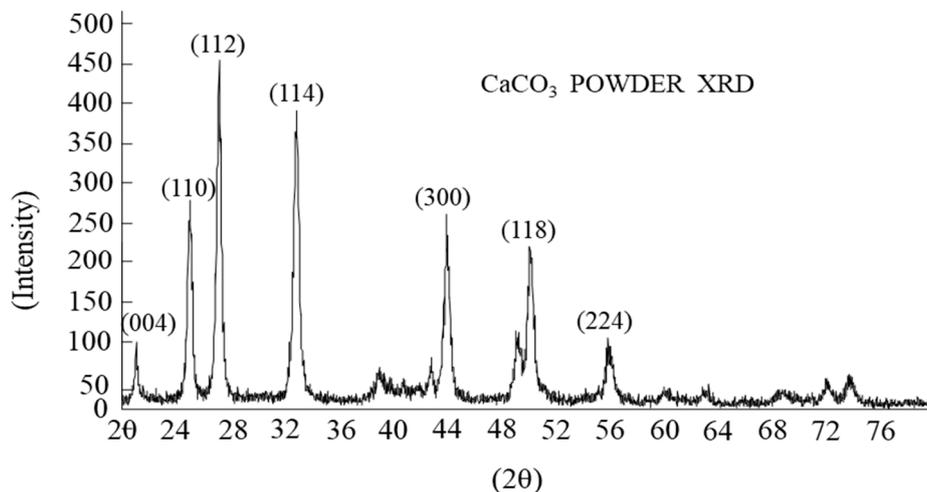
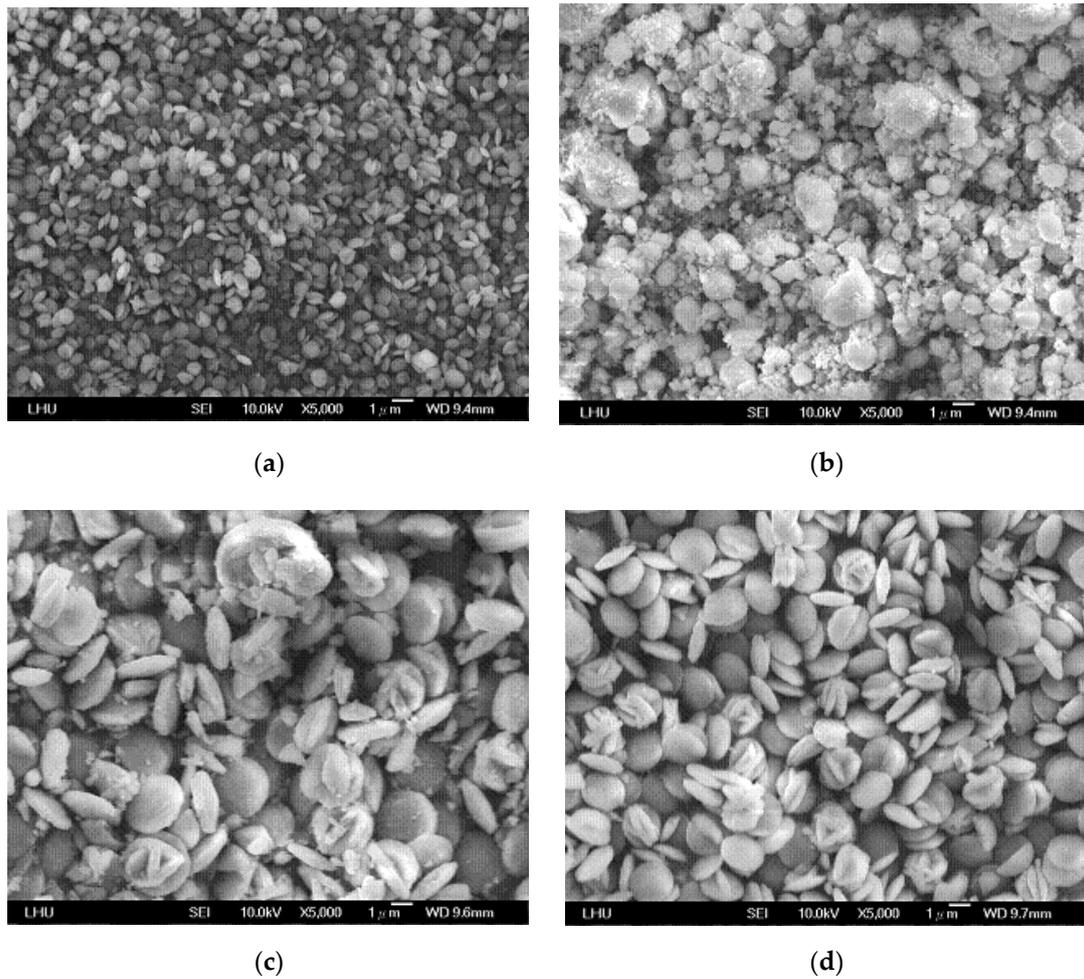


Figure 3. XRD spectra for No. 2 showing the intensity of vaterite.

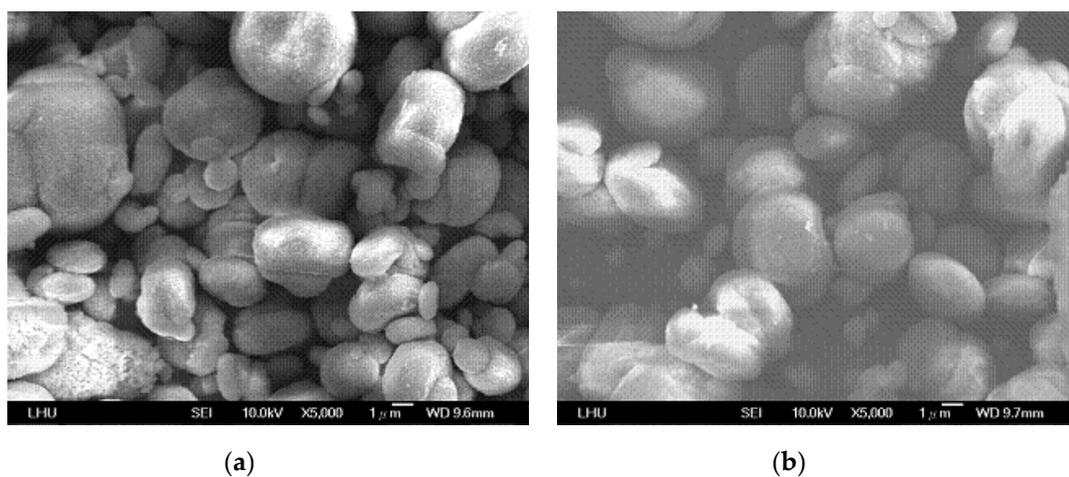
#### 4.3. Effects of Variables on Vaterite Morphology and Size

Figure 4 shows different morphologies of vaterites with different flow rates observed by SEM when the pH was 9 and  $y_1$  was 10%. According to the images observed by SEM, the single particles were mainly disc vaterites. With the increase in  $Q_g$ , the morphology changed a little, but the particle size decreased. The picture in Figure 4a showed the uniform particles were observed; on the other hand, in Figure 4b–d, they showed some tiny particles were formed giving average size smaller. However, the effects of  $Q_g$  on particles need to be investigated further. Figures 4b and 5 show the effects of different  $\text{CO}_2$  concentrations on the vaterite morphology; the morphology obtained at different  $\text{CO}_2$  concentrations was nearly discoid and spherical. Its morphology was nearly spherical when  $y_1$  was 10% ( $d_p = 1.33 \mu\text{m}$ ), 20% ( $d_p = 1.63 \mu\text{m}$ ), and 30% ( $d_p = 1.65 \mu\text{m}$ ), and the mean particle size increased with the increase in  $y_1$ .

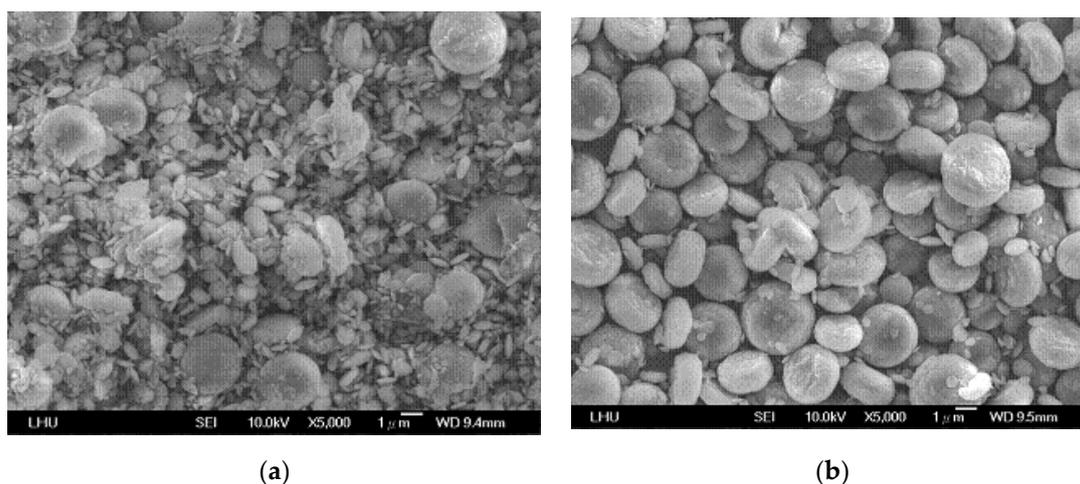
Figures 4b and 6 show the different morphologies at different pH values when  $y_1$  was 10% and the flow rate was 4.0 L/min. At pH 9, as shown in Figure 4b, the calcium carbonate morphology was roughly spherical; at pH 10, spherical crystals began to form; at pH 11, the morphology was mainly spherical and significantly exhibited the shape of vaterite, and the particle size increased with the increase in pH value. However, when  $y_1$  was 20% and 30%, the particle size decreased with the increase in pH (Please see Table 2). The possible reason may be that the increase in MEA feed and  $\text{CO}_2$  absorption at a high pH improved the rates of supersaturation and nucleation, so that the precipitation increased accordingly, which affected the particle size and morphology.



**Figure 4.** Effects of  $Q_g$  on the morphology and crystal size of vaterite. (a)  $Q_g = 2$  L/min ( $d_p = 1.60$   $\mu\text{m}$ ) (No. 1); (b)  $Q_g = 4$  L/min ( $d_p = 1.33$   $\mu\text{m}$ ) (No.4); (c)  $Q_g = 6$  L/min ( $d_p = 1.14$   $\mu\text{m}$ ) (No. 7); (d)  $Q_g = 8$  L/min ( $d_p = 1.01$   $\mu\text{m}$ ) (No. 10).



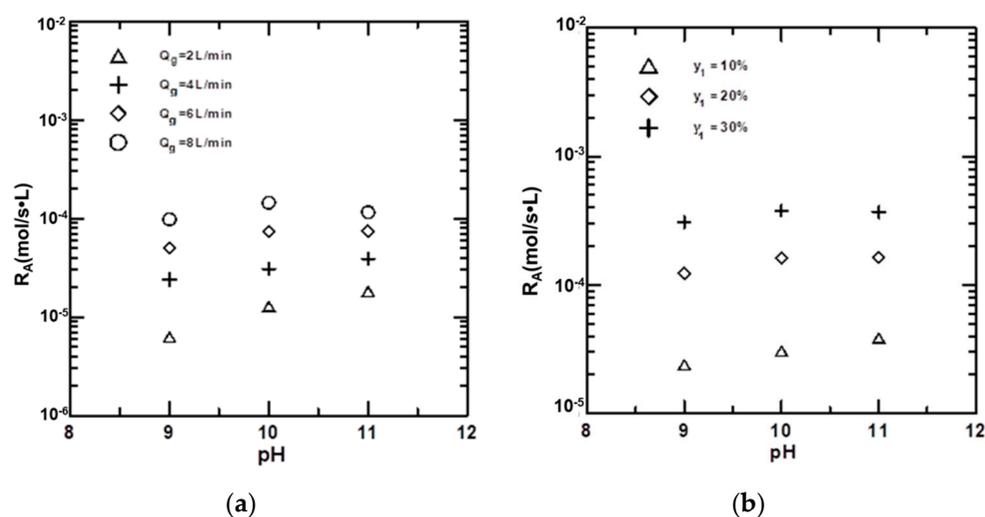
**Figure 5.** Effects of  $\gamma_1$  on the morphology and crystal size of vaterite (pH = 9,  $Q_g = 4$  L/min). (a) 20% ( $d_p = 1.63$   $\mu\text{m}$ ) (No. 13); (b) 30% ( $d_p = 1.65$   $\mu\text{m}$ ) (No. 16).



**Figure 6.** Effects of pH on the morphology and crystal size of vaterite ( $y_1 = 10\%$ ,  $Q_g = 4\text{L/min}$ ). (a) pH = 10 ( $d_p = 1.41\ \mu\text{m}$ ) (No.5); (b) pH = 11 ( $d_p = 1.83\ \mu\text{m}$ ) (No. 6).

#### 4.4. Effects of Variables on the Absorption Rate of $\text{CO}_2$

To investigate the effects of variables on the absorption rate, the pH value at the absorption rate ( $R_A$ ) was drawn, as shown in Figure 7. In Figure 7a, with the volume flow rate as the parameter,  $R_A$  was found to increase roughly with the increase in pH;  $R_A$  increased linearly with pH at low flow rates and remained steady with the increase in pH at high flow rates, indicating that the increase in pH had limited effects on the absorption rate. In addition, Figure 7a also shows that, at high flow rates, the absorption rate was high and increased significantly, indicating that increasing the flow rate is an effective method to increase the absorption rate. Finally, as per Figure 7b, the feed concentration significantly increased the absorption rate, but the effects of pH were limited at high values of  $y_1$ .



**Figure 7.** Effects of process variables on the absorption of  $\text{CO}_2$ . (a) Effects of pH at different gas-flow rates; (b) Effects of pH at different gas concentrations.

The effects of parameters on  $R_A$  were explored using linear regression and the result was as follows:

$$R_A = 6.9095 \times 10^{-5} \exp(0.21pH) y_1^{2.12} u^{1.67} \quad (13)$$

The regression error was 1.63%. The regression confidence is shown in Figure 8. The regression result showed that  $R_A$  was proportional to  $u$  and  $y_1$  to the powers of 1.67 and 2.12, respectively. It also shows that  $R_A$  increased with an increase in pH. In addition, the  $R_A$  values presented here were in

the range of  $0.063 \times 10^{-4}$ – $3.8 \times 10^{-4}$  mol/s·L, which was much smaller than that of MEA-CO<sub>2</sub>-H<sub>2</sub>O absorption system ( $3.68 \times 10^{-4}$ – $56.8 \times 10^{-4}$  mol/s·L) as reported in the previous study [21]. The difference was due to the formation of vaterites, a larger number of tiny particles, which enhanced the coalescence of the bubbles. Due to this, the mass-transfer rate of CO<sub>2</sub> gas was blocked, which reduced the absorption rate.

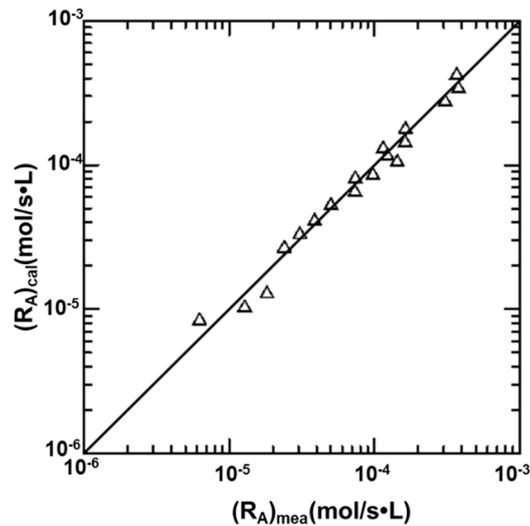


Figure 8. Regression confidence for  $R_A$ .

#### 4.5. Effects of Variables on $K_{GA}$

As shown in Figure 9a, the  $K_{GA}$  value increased linearly with the increase in pH, and a higher gas flow rate led to a higher  $K_{GA}$  value. At a high pH value (pH = 11), the absorption tended to be complete, as shown in Figure 2, indicating the reduced effects on  $K_{GA}$ . Figure 9b shows that  $K_{GA}$  increased with the increase in pH and  $y_1$ , and this value was large at a high pH. The figure also shows that, at pH = 10 and 11, the  $K_{GA}$  values were leveled off, indicating the diminishing effects of pH.

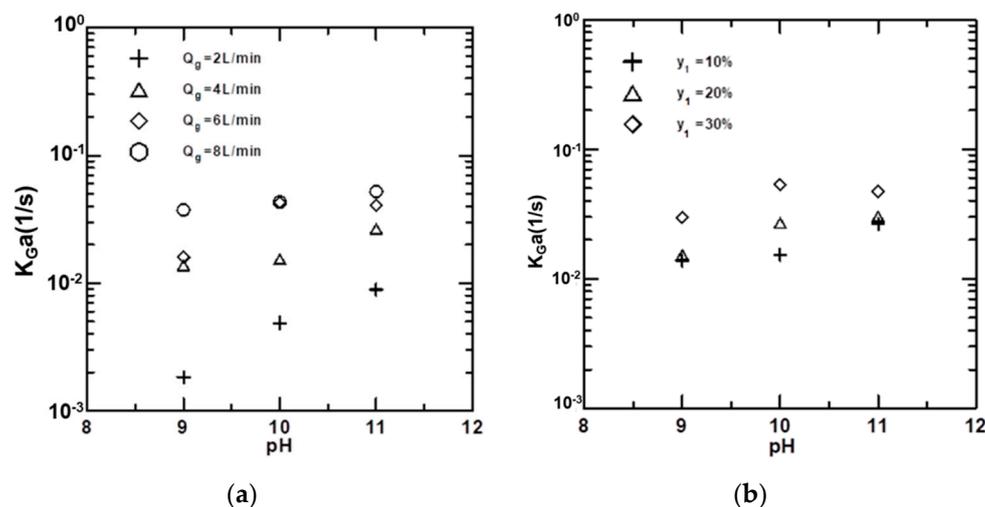


Figure 9. Effects of variables on the  $K_{GA}$  at different conditions. (a) Effects of pH at different gas-flow rates; (b) Effects of pH at different gas concentrations.

The relationship between  $K_{GA}$  and pH value, and between  $u$  and  $y_1$  was explored, and  $K_{GA}$  was used to carry out a regression analysis of  $u$ ,  $y_1$  and pH, and the result was as follows:

$$K_{GA} = 2.8469 \times 10^{-4} u^{1.68} y_1^{0.87} \exp(0.39pH) \quad (14)$$

The regression error was 6.42%. The difference between the calculated value and the measured value is presented in Figure 10. The regression result showed that  $K_{GA}$  was proportional to  $u$  to the power of 1.68 and the obtained value was closer than that reported earlier, which was between 0.58 and 1.67 [7,9–12], and the empirical formula also shows that  $K_{GA}$  increased with the increase in  $y_1$  and pH value. The overall mass transfer coefficients at different pH values,  $y_1$ , and  $u$  could be estimated from Equation (14), and after the values were determined, the volume of the absorption tower could be estimated. In addition, the difference in the mass transfer coefficient in the bubble columns can be compared with each other. For example, please see Table 3. The values obtained in this study ranged from 0.01 to 0.15 1/s, congruent with those reported in the literature [29–33]. However, these values were much smaller than those reported in previous work [21], and those by Al-Naimi et al. [29]. In our study, as shown in Table 2,  $K_{GA}$  decreased with an increase in  $F_p$ , such as that in No.1-No.3. In addition, in other earlier studies [23] we found that Nos. 7(0.0136 1/s), 8(0.0199 1/s), 10(0.0506 1/s), 11(0.0299 1/s), 12(0.0241 1/s) were lower in mass-transfer coefficient due to the formation of ABC crystals. This decrease in mass transfer coefficient with increasing solid concentration is attributed to a decrease in small bubble and an increase in large bubble sizes due to the bubble coalescence tendencies, and they exhibited limited the mass transfer coefficient [29]. A similar trend was found in an earlier study [31].

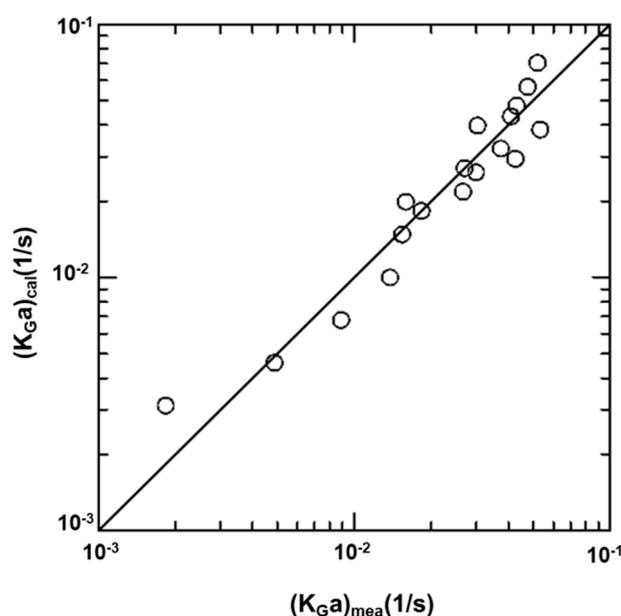


Figure 10. A plot of calculated  $K_{GA}$  versus measured  $K_{GA}$ .

Table 3. Comparison of mass-transfer coefficients in the bubble columns.

$K_{GA}(1/s)$	$R_A \times 10^4(\text{mol/s}\cdot\text{L})$	Remarks and References
0.01–0.14	-	$O_2$ -Liquid(water/glycerin/alcohol)-Solid(PVC) [29]
0.045–0.085	-	$O_2(N_2+O_2)$ - $H_2O$ [30]
0.02–0.14	-	Air-Paraffin oil-Porous catalyst [31]
0.01–0.15	-	$O_2$ - $H_2O$ [32]
0.0377–0.8881	3.68–56.8	$CO_2$ -MEA- $H_2O$ [21]
0.021–0.109	1.36–6.61	$CO_2$ -NaOH- $H_2O$ [33]
0.0143–0.3302	3.21–9.03	$CO_2$ - $NH_3$ - $H_2O$ [23]
0.0183–0.0520	0.063–3.80	$CO_2$ -MEA- $CaCl_2$ - $H_2O$ [This work]

#### 4.6. Precipitation Rates of Vaterites

Figure 11 shows the relationship between the rate of  $CaCO_3$  precipitation and pH at different  $y_1$ . The results indicate that the precipitation rate of  $CaCO_3$  increased with the decrease in pH, otherwise,

the precipitation rate decreased. This figure also shows that  $F_p$  tended to increase with an increase in  $y_1$ . Figure 12 shows the effects of pH on  $F_p$  at different  $Q_g$  values and obviously indicates that  $F_p$  values decreased with the increase in pH, regardless of  $Q_g$ . Moreover, generally, a higher  $Q_g$  led to a larger  $F_p$ . However, when  $Q_g = 8$  L/min, except at pH = 9,  $F_p$  was smaller than that at  $Q_g = 6$  L/min, which may be caused by the restriction of the system operation.

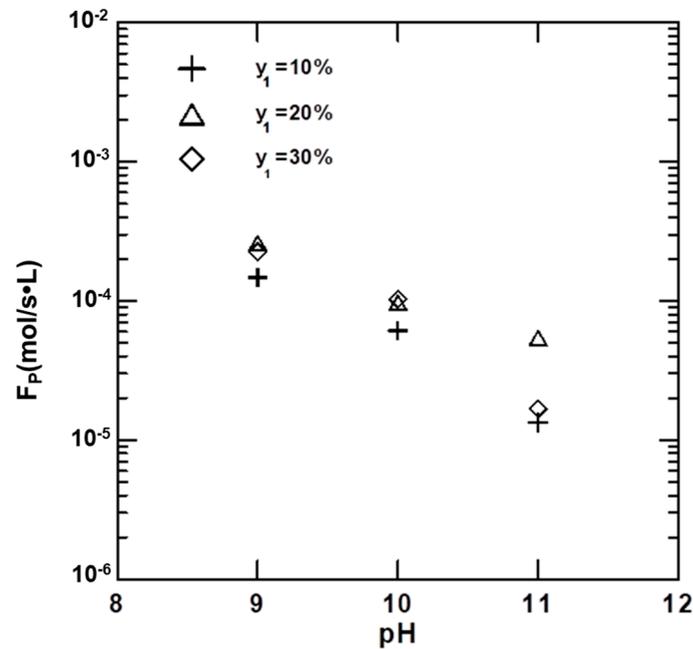


Figure 11. Variation in  $F_p$  with pH at different  $y_1$  values.

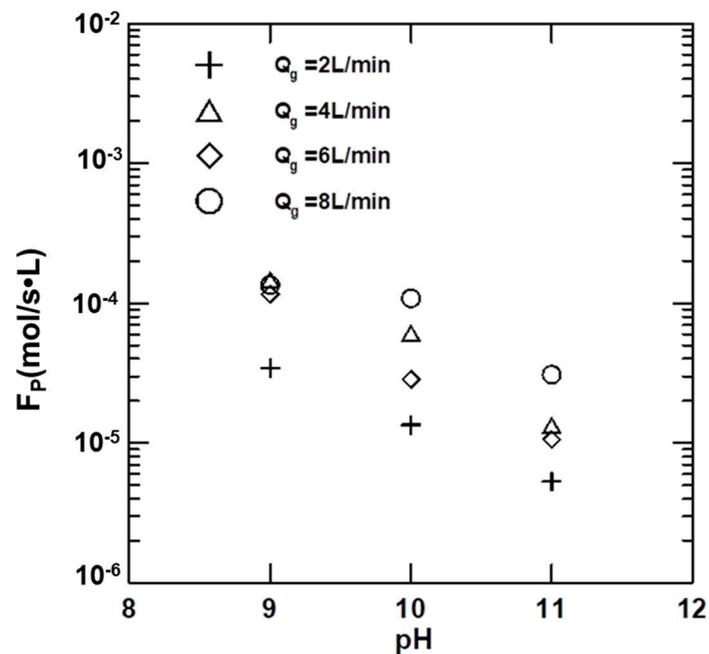


Figure 12. Variation in  $F_p$  with pH at different  $Q_g$  values.

The results of the above discussion and the data in Table 2 indicate a competition effect between  $R_A$  and  $F_p$ , which was affected by  $u$ ,  $y_1$ , and  $pH$ . Hence,  $F_p$  was used to carry out the regression of parameters for comparison, and the result was as shown below:

$$F_p = 2.5081 \exp(-1.02pH) y_1^{0.98} u^{1.06} \quad (15)$$

The error was 4.28% and the reliability was as shown in Figure 13. According to this equation, the  $F_p$  value decreased with the increase in  $pH$  and increased with an increase in  $u$  and  $y_1$ . Here, we defined the ratio of  $R_A$  and  $F_p$  as  $\psi$ . Using Equations (13) and (15), the relation became  $\psi = 2.7548 \times 10^{-5} \exp(1.23pH) y_1^{1.14} u^{0.61}$ . A high  $\psi$  value indicates that the mass transfer was dominated by absorption, while a low  $\psi$  value indicates that the mass transfer was dominated by crystallization.

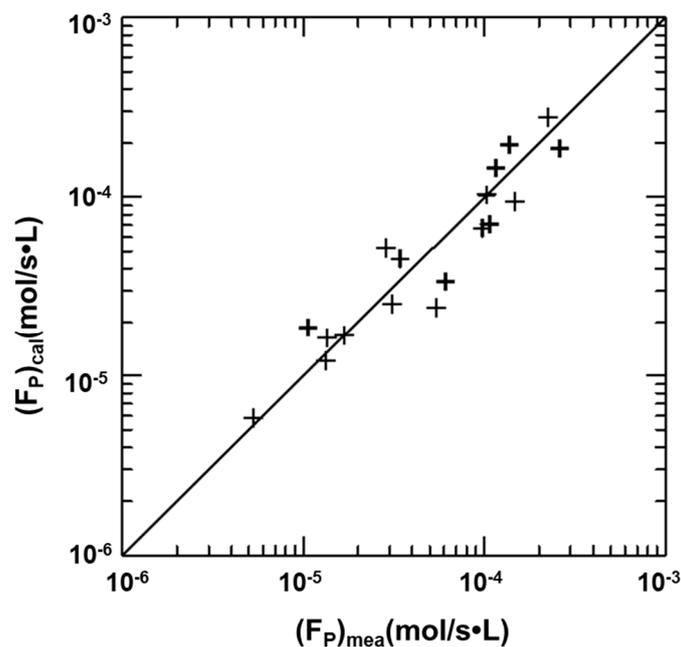


Figure 13. A plot of calculated versus measured  $\psi$  showing the confidence of regression.

## 5. Conclusions

In a continuous bubble column, the vaterite was precipitated mainly in disk-like and spherical morphology if MEA/CaCl<sub>2</sub>/H<sub>2</sub>O solution was used for CO<sub>2</sub> absorption. At  $pH = 11$ , regardless of the other conditions, the absorption rate was close to 100%, so the increase in  $pH$  made no contribution to the improvement in absorption efficiency. The shell balance and two-film model were able to determine the absorption rate and overall mass transfer coefficient. An improvement in the gas flow rate and gas concentration increased the solid precipitation rate and overall mass transfer coefficient, but the solid precipitation rate decreased with the increase in  $pH$  values. Therefore, the precipitation rate was competitive with the absorption rate, which could be estimated by  $\psi (= R_A/F_p)$ . A high  $\psi$  value indicates that the mass transfer was dominated by absorption, while a low  $\psi$  value indicates that the mass transfer was dominated by crystallization. The results show that the MEA/CaCl<sub>2</sub>/H<sub>2</sub>O solution can be used to absorb CO<sub>2</sub>, the greenhouse gas, and recover CaCO<sub>3</sub>, and is a technology worthy of further development.

**Author Contributions:** P.C.C. conceived and designed the experiments and wrote the paper, while S.H.Z. performed the experiments and analyzed the data. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research received no external funding.

**Acknowledgments:** The authors acknowledge the financial support of the MOST in Taiwan ROC (MOST-109-2221-E-262-004).

**Conflicts of Interest:** The authors declare no conflict of interest.

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