Modeling of Bubble Column Reactor in up gradation of waste calcium carbonate using carbonation process

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Abstract --The kinetics of absorption of lean CO_2 in a suspension of lime is studied in 8.0 cm. i.d. bubble column. The various variable studies are height to diameter ratio (h/d) , superficial gas velocity of mixture of CO_2 –air. The final optimal experimental condition are done by employing height to diameter ratio (h/d) equal to 6, superficial gas velocity (Vg) equal to 10.Under this experimental conditions, required particle size of less than 10μm of calcium carbonate is obtained.
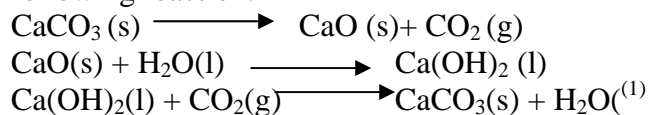
A mathematical model for absorption of CO_2 has been used to predict interfacial area and liquid- side mass transfer coefficient KL is found out by using Experimental Ra absorption of CO_2 and interfacial area. The liquid- side mass transfer coefficient in bubble column reactor is determined and found to be $0.21*10^{-2}$ cm/ sec.

I. INTRODUCTION

Calcium Carbonate is available in two forms, Precipitated and activated.

Precipitated calcium carbonate is available in calcite and aragonite crystal forms and further calcite grade is available also as stearate coated activated grade.

Precipitated calcium carbonate is made from calcining the high quality limestone into burned lime, slaking   and carbonating. This is the general method practiced.   Waste   lime   is calcinated to form burned lime, which is slaked and carbonated. These are represented by the following reaction.

$CaCO_3 (s) \longrightarrow CaO (s) + CO_2 (g)$

$CaO(s) + H_2O(l) \longrightarrow Ca(OH)_2 (l)$

$Ca(OH)_2(l) + CO_2(g) \longrightarrow CaCO_3(s) + H_2O$ (1)

II. EXPERIMENT

The complete experimental set up for carbonation of calcium carbonate is equipped with the bubble column reactor. It consists of Carbon- dioxide cylinder and compressor.

Bubble column experimental apparatus used in the study is made by glass. The diameter of bubble column reactor is 8cm. and height is 140cm. The reactor is fitted with a orifice gas sparger placed at 20 cm. height from the bottom of the reactor. Bubble column reactor uses orifices for introducing the gas to ensure better gas distribution. In this case the orifice may be holes from 3 m.m in diameter. The diameter of the orifice gas sparger is 6 cm. and around 12 holes. Sparger located at the bottom of the reactor may simply be an open tube through which the gas issues into the liquid. The reactor is also equipped with thermocouple which at 55 cm. height from the bottom of the reactor. Thermocouple gives the correct temperature when carbonation is going on. It is also equipped pH meter at 45c.m. height from the bottom of the reactor that gives the pH during carbonation. The reactor has inlet for mixture of carbon   dioxide-air   through   sparger. Arrangement has been made to cool bubble column reactor during carbonation. The reactor has outlet for undissolved CO_2 that has negligible pressure so it is not noted.

For performing carbonation, CO_2 is passed from CO_2 storage cylinder through rotameter and pressure guage. Air is also passed from compressor through rotameter and pressure. The capacity of bubble column reactor for carbonation is 7000ml. The sample at regular interval can be withdrawn from sampling valve.

Raw material: -

In the experiment, we use GNFC waste lime as raw material.

1) Calcination

The waste lime is calcinated at 900^0C in muffle furnace. The muffle furnace takes two hours for reaching temperature of

900^0C then keeping constant temperature of 900^0C for 90 minutes and then cooling from 9000C to 100^0C. Cooling from 900 ^{0}C to 1000 ^{0}C also required 6 hours. After calcinations from waste lime CO_2 is evolved & we get CaO. Then CaO is pulverised with hammering and grinding and then passed through 150 mesh to get fine powder of CaO which is used for slaking. Now this calcinated mass or CaO is taken as per requirement like 250 gm 300 gm in 1250 ml & 2500 ml respectively.

2) Slaking

During slaking we maintain 20% slurry concentration. According to that we take calcinated mass & water for slaking. During this agitation is provided by disk type agitator. Slaking takes 1 hrs. Then measure temperature at some time interval using thermocouple. For the carbonation we use 10% slurry. So dilute that slurry using the water. Then measure the temperature & pH.

3) Carbonation

The solution $Ca(OH)_2$ is stirred before carbonation and is kept for half hour at room temperature. After that taking this slurry in a reactor for carbonation.

The experiments are conducted with employing CO_2 and air mixture. The require flow of CO_2 is then passed from CO_2 storage cylinder through pressure regulator & also compressed air is passed from compressor through pressure regulator to the inlet valve. This CO_2 - air mixture is passed through sparger to initiate the carbonation in the bubble column reactor.

The pH of the solution is initially found to be around 10-12 . As carbonation proceeds, pH of the solution decreased up to 7 pH that indicate the completion of reaction. We pass CO_2 –air upto equilibrium pH. Then stop the flow rate of CO_2&passed only air some time. Then check pH is same or increase. Increase in pH indicate that carbonation is not complete. ThenstartCO2againforsome time means upto7 pH. This procedure follows upto equilibrium pH is reached. In this carbonation air serves as agitation medium. When the operation of carbonation is complete, carbonated mass is filtered using vacuum filtration. The cake

obtained is kept in oven for 4 to5hours at 110 ^{0}C. After dying the cake is weight and pulverize.[1]

The pulverized material is then passed from 150 mesh for particle size distribution analysis The particle size distribution is analyzed using computerized Hydro 2000 SCA PSD analyzer in which ultraviolet rays are used to analyze the sample. Sample of 1.2 gms is taken in the PSD analyzer for 2-3 minutes. The result of PSD is seen on the computer screen.

III. EXPERIMENTAL RESULT

The effect of gas velocity 10 c.m / sec at h/d =6 given

Time (min)	Temp (C)	PH	Pressure (lb_f)	% CO_2 orsat	% CaO
0	29	11.64	7		81%
3	30	11.00	8.5		
5	31	10.63	11		
13	32	10.60	17	9 %	66.30%
15	3	10.55	17		
18	33	10.79	17		
22	34	10.96	16		
25	34	11.00	15		
26	34	11.04	15		
27	34	10.94	15	11%	4.5%
30	35	10.73	15		
32	33	10.41	15		
33	33	7.71	15		
34	33	7.00	15	18%	18.94%
35	31	6.46	15		
38	29	6.41	15		
43	28	7.39	15		
44	28	6.71	15		
47	28	7.12	15		3.5%

IV. MODELING

In the carbonation of calcium hydroxide using pure CO_2

Following resistance are involved
1) Resistance through the gas film.
2) Resistance through the solid –liquid film.
3) Resistance through the liquid film where the absorption of CO_2 is accompanied by a relatively fast reaction

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The rate of various steps can be written as follows:

1) Rate of transport CO_2 through the gas film
   $$Ra = K_G a (P_g - P_i) \quad \ldots\ldots\ldots\ldots (1)$$

2) Rate of dissolution of lime
   $$Ra = K_s a_P V([Bs] - [B_0])/Z V_d \quad \ldots.. (2)$$

3) Rate of transport of CO2 in to the liquid and the reaction of CO2 with hydroxyl icon.

The transport of CO_2 in the liquid accompanied by fast reaction have given a comprehensive account of kinetics of the reaction between CO_2 and OH ions. It is cleared from the work that the rate of CO_2 will be considerably enhance due to the reaction between CO2 and OH ions.

$$Ra = \frac{Gms\ of\ CO2\ utilized}{Mol.\ wt\ of\ CO2 * Volume\ of\ sample * time}$$

Gms CO2 obtained is calculated from the CaCO3 formed in carbonation experiment study where slurry in c.c and time in sec. Under certain circumstances of OH ions at the gas-liq. Interface may be the same as that in the bulk and the reaction may occur entirely in the film. The following equation will held:

$$Ra = [A^*] a \sqrt{D_A K_2 [B_0]} \quad \ldots. (3)$$

The necessary conditions to be satisfied are

$$\frac{\sqrt{D_A K_2 [B_0]}}{K_L} \gg 1 \quad \ldots (4a)$$

And

$$\frac{\sqrt{D_A K_2 [B_0]}}{K_L} \gg \frac{[Bo] \sqrt{D_B/D_A}}{Z[A^*]} \quad \ldots (4b)$$

$[A^*]$ = Solubility of CO2 in aqueous phase g mole/cm3 liquid and is given by

$$[A^*] = H * Pi \quad \ldots (5a)$$

Eliminating $[A^*]$ and Pi from (1), (3) and (5) we get

$$Ra = \frac{a\ H\ Pg\ \sqrt{D_A K_2 [Bo]}}{1 + a\ \frac{H \sqrt{D_A K_2 [Bo]}}{K_G a}} \quad \ldots. (6)$$

Under certain circumstances the condition given by expression (4b) may be satisfied but that given by expression (4a) may not be satisfied. For instance the condition given by expression (4a) may not be satisfied for low values of [Bo] and relatively high value of KL

$$\frac{\sqrt{D_A K_2 [Bo]}}{K_L} = 1 \quad \ldots. (7)$$

When the condition given by expression (4a) is not satisfied it implies that a part of the reaction between CO2 and OH occurs in the film and the rest in the bulk liquid.

The following condition is satisfied.

$$\frac{Ks\ a_p [Bs]}{Z} \gg \frac{a\ H\ Pg\ \sqrt{D_A K_2 [Bs] + K_L{}^2}}{1 + aH \frac{\sqrt{D_A K_2 [Bs] + K_L{}^2}}{K_G a}} \quad \ldots. (8)$$

And the rate of absorption of CO_2 is given by

$$Ra = \frac{a\ H\ Pg\ \sqrt{D_A K_2 [Bs] + K_L{}^2}}{1 + a\ H\ Pg\ \frac{\sqrt{D_A K_2 [Bs] + K_L{}^2}}{K_G a}} \quad \ldots. (9)$$

The condition given be expression (7) and (4a) are satisfied. The rate of CO2 absorption is therefore given by eqn. (8). Since the gas-film resistance to the transfer of CO2 is negligible. Eqn. (9) reduces to the from

$$Ra = a\ H\ Ptm\ \sqrt{D_A K_2 [Bs] + K_L{}^2} \quad \ldots. (10)$$

Calculation of liquid solid mass transfer coefficient in Bubble column reactor:

a)   Determination of K_La[2]

The value of in bubble column were obtained by carrying out the absorption of CO_2 in an aqueous buffered solution of Na_2CO_3-$NaHCO_3$ (ionic strength = 2 gion / l) in which calcium carbonate particle were suspended. The ratio of CO_3^{2-} ions and HCO_3^- ions kept equal to 1. Under these conditions.

$$Ra = K_La \ H \ Ptm \qquad ------(11)$$

Calculation of liquid side mass transfer coefficient in Bubble Column Reactor : -For calculation mass transfer coefficient , K_L in Bubble Column reactor, Knowing the value of gas liquid interfacial area a which can be found out by formula.

$$Ra = \frac{a \ H \ Pg \ \sqrt{D_A \ K_2 \ [Bo]}}{1 + \frac{a \ H \ \sqrt{D_A \ K_2 \ [Bo]}}{KGa}}$$

Where

H = 2.88 * 10-5 g mole / cm^3 atm, Da = 2.1 * 105 cm^2 / sec, $K2$ = 1.24 * 104 lit / mole sec, Bo = 4 * 105 g ion / cm^3

Pg = 1.47 atm, Ptm = 1.21 atm , KGa = 5 * 10-5 mole /cm^3 sec atm, Putting all the values in given formula give interfacial

a = 3.8 Cm^2 / Cm^3 Slurry

And the rate of absorption of CO2 is given by

$$Ra = a \ H \ Ptm \ \sqrt{D_A \ K_2 \ [Bs] + K_L^2}$$

In above formula putting values of a, and other values liquid side mass transfer coefficient can be calculated and comes as 0.21 *102 cm / sec

The values are as follows:

Vg Cm/sec	Ra mole/cm³ sec	Pg atm	Ptm atm	K_L Cm/sec
10	$5.2*10^{-7}$	1.44	1.21	$0.21*10^{-2}$
12.5	$3.7*10^{-7}$	1.61	1.27	$0.249*10^{-2}$
15	$1.85*10^{-7}$	1.81	1.357	$0.289*10^{-2}$

V CONCLUSION

Mathematical model for CO_2 absorption in lime slurry is used to obtain the values of interfacial area and K_La. It is found both a and K_La has been found to be constant for the superficial gas velocity used in the carbonation experiment.

NOMENCLATURE

[A*]   Solubility of carbon dioxide in an aqueous solution, g mole / cm^3

a   Effective gas-liquid interfacial area cm^2/ cm^3 of dispersion

a_p Solid-liquid interfacial area, cm^2/ cm^3

[Bo]   Concentration of OH^- ions at the bulk liquid phase, g ion/ cm^3

[Bs]   Saturation concentration of OH^- ions in aqueous solution in equilibrium with $Ca(OH)_2$(solid), g ion/ cm^3

D_A Diffusivity of CO2 in aqueous solution cm^2/sec

D_B Diffusivity of OH^- ions in aqueous solution cm^2/sec

H   Henry's coefficient of solubility, g mole/ cm^3atm

K_G Gas- side mass transfer coefficient, mole/ cm^2 sec atm

K_L Liquid- side mass transfer coefficient, cm/ sec

K_1 Pseudo first order rate constant, sec^{-1}

P_g Partial pressure of CO_2 in gas steam, atm

Pi   Partial pressure of CO_2 at the gas-liquid interface, atm

Ptm   Log mean partial pressure of CO_2, atm

R   Specific rate of absorption of CO_2, mole/ cm^3 sec

VI. REFERENCES

[1] B.A.V.K Sharma, 8 July 1997 "Precipitated calcium carbonate, Theory and manufacture from low grade limestone and a project profile", Chemical Weekly, 155-160

[2] V.A Juvekar and M.M Sharma, 1973 "Absorption of CO2 in Suspension lime", Chem. Eng. Sci., **28**, .825-837

[3] Wachi s and Jones A.G, 1991, mass transfer with chemicals reaction & precipitation" Chem. Eng. Sci., **46** , 1027-1023

[4] Kirk-Other encyclopedia of chemical technology calcium compound to chloramphenicol, **4**, 1-11