Effect of Different CO_2 Flowrate and Calcium Chloride Concentration on The CO_2 Hydration Using Carbonic Ion Solution

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Abstract—**The carbon dioxide emission has been increased which can cause the global warming and other environmental impacts. The carbon sequestration process has been introduced as one of the method to reduce the amount of carbon dioxide in the atmosphere. Through mineral carbonation, carbon dioxide is stored in form of stable mineral carbonate such as calcium or magnesium. In this research, the mineral carbonation was performed by using carbonic ion solution which accelerated by carbonic anhydrase enzyme. Two parameters were being studied which are the effect of the CO_2 flowrate and $CaCI_2$ concentration towards hydration process of CO_2**

Keywords— ***CO2 hydration, Carbonic ion solution, Carbon Sequestration, Mineral Carbonation, Carbonic Anhydrase, Immobilization, Polyvinylidene fluoride (PVDF)***

I. INTRODUCTION

The carbon dioxide (CO_2) emission has been increased to the environment due to the industrial growth. The carbon dioxide emission is mainly caused by the combustion of fossil fuels and the industrial growth itself. The carbon dioxide (CO_2) is known as greenhouse gases that contribute to the environmental issue like greenhouse effect and also climate change around the world.

The carbon capture and storage techniques has been introduced to capture the carbon dioxide produced and prevent it from being emitted to the atmosphere. Hence, the amount of the greenhouse gases including the carbon dioxide could be reduced. In this technologies chain, there are consists of three part which are capturing the CO_2, transporting the CO_2 and storing the CO_2 in underground like in the depleted oil and gas wells or in deep saline aquifer formation. In capturing the CO_2, there are several technologies has been employed such as post combustion capture, pre-combustion capture and oxygen fuel combustion. While, CO_2 transportation can be done via pipelines or ship tanker and it depends on the distance between two places. [1] For the storage of carbon dioxide, several options being highlighted like geological storage, ocean storage and the several options are being highlighted like geological storage, ocean storage and the mineralization. In the ocean storage, the carbon dioxide was injected at very deep depth in the ocean. The injected carbon dioxide was dissolved and formed the hydrate which heavier than water plume. The hydrate will be settles down in the bottom of the sea. The geological storage, the carbon dioxide can be stored in the place like depleted oil and gas reservoir, saline aquifer and unminable coal. However, there are limitations for both geological and ocean storage. For the ocean storage, the carbon dioxide rise of carbon dioxide concentration will cause the acidification that can affect the marine life and also interrupt to the coral growth rate. Meanwhile, the leaking is the problem in the geological storage. The leaking of the carbon dioxide can cause the change of the water PH, affect the human health and bring death to the animal. Besides, the injection of the carbon dioxide near to the water source can affect the potable ground water source.

The other option for the carbon dioxide storage is carbon sequestration. It so-called long-term carbon dioxide storage which could reduce the amount of carbon dioxide in the atmosphere. The carbon dioxide sequestration by mineral carbonation is the technique which produce the carbonate from the mineral that consist of calcium and magnesium that been react with the carbon dioxide. [2]. There several types of stable carbonate such as calcite as $CaCO_3$, dolomite as $CaO.5MgO\cdot5CO_3$, magnesite as $MgCO_3$ and siderite as $FeCO_3$.

The mineral carbonation has two types which are in-situ carbonation and ex-situ carbonation. In-situ carbonation occurs. When the magnesium and calcium mineral in underground was reacted with injected carbon dioxide. While ex-situ carbonation reaction is same as in-situ carbonation but it takes place above the ground. The formation of calcium carbonate gets interest since it is having been used as material in polymer industry [3].

As been mentioned earlier, many options of the carbon dioxide storage have been proposed such as geological storage and ocean storage and also mineral carbonation. Unfortunately, both the geological and ocean storage has the drawbacks towards environment, economic and social. The mineral carbonation is preferred as it offer the long-term storage of carbon dioxide gas into the mineral carbonate such as calcium or magnesium carbonate which has commercial value. So, in this research, the capturing carbon dioxide will be performed using the CO_2 hydration using the carbonic ion solution which accelerated by biocatalyst carbonic anhydrase enzyme. The objectives of this research are to study the reduction of the CO_2 gas using different concentration of calcium chloride and to study the morphology of calcium carbonate precipitate using Scanning Electron Microscope(SEM), X-Ray Diffractometer (XRD) and Fourier Transform Infrared Spectroscopy (FTIR) analysis.

II. METHODOLOGY

A. *Materials*

This study conducted using the calcium chloride purchased from Systerm, while the bovine carbonic anhydrase enzyme 35 KDA unit/mg protein (3.5 mm in size) was purchased from Sigma Aldrich. The carbon dioxide gas 100% purity is as source of carbonate ion was purchased from Polygas. For the immobilization of enzyme, the Tris-buffer used was purchased from Sigma Aldrich and Glutaraldehyde was purchased from Merck. The support membrane for enzyme immobilization used is Polyvinylidene fluoride (PVDF)

B. Immobilization of Bovine Carbonic Anhydrase (CA) onto membrane support

i. Preparation of buffer (pH 8, 50 mM)

1.51 g of buffer was diluted with distilled water into 250 ml volumetric flask. The nitric acid was added to adjust the pH until the pH 8 was obtained.

ii. Preparation of 1% Glutaraldehyde (GA)

4 ml of glutaraldehyde was taken from the original stock that have concentration 25% and added with distilled water until reached graduation mark of the 100 ml of volumetric flask to form 1% of GA concentration.

iii. Preparation of enzyme solution

0.01 g of Bovine Carbonic anhydrase enzyme was weighed and put on the beaker. The 5 ml of 50 mM buffer was added to the CA enzyme powder. The membrane support with 3 cm size was rinsed with distilled water and put into the beaker. Then, the beaker was placed in the water bath at temperature 37℃ at 100 rpm for 2 hours. Then, the glutaraldehyde was added and the beaker was shaken for another 2 hours. Lastly the membrane support was take out and rinse with tris buffer and room dried for further used.

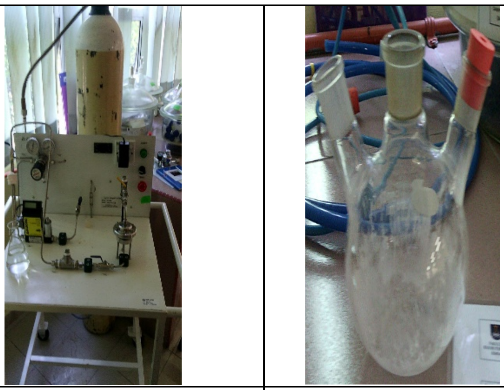
C. Hydration process of CO_2 using membrane CO_2 rig

Firstly, the rig was set up at illustrate at Figure 1. The setting was made for flowrate and temperature using the controller at membrane co2 rig. Then, the membrane support with 3 cm size that been put in the holder. Setting of membrane co2 rig was tabulated in the table 1.

Table 1: the membrane co2 rig settings

Settings	value
Fowrate, L/min	200, 500 and 800
Temperature, ℃	30

Next the tris-buffer was prepared in 200 ml volumetric flask.1.21 g of Trizmase buffer was diluted with distilled water in the beaker. Then the, the buffer was transfer to the volumetric flask. The water was added until to the graduation mark was reached. Then, 4.86 g of calcium chloride was weighed and mixed with buffer in the flask. The carbon dioxide was flow through the solution containing the calcium chloride and tris buffer The Ph reduction was observed using the PH meter. The reaction was stopped when PH was obtained was time was recorded. The cloudy solution which contains calcium carbonate precipitate was filtered using the filter paper. The precipitate was dried for a day to obtained the white calcium carbonate powder and proceed with analysis



The gas membrane and CO_2 gas source

flask

Figure 1: The arrangement of rig for CO_2 sequestration

D. Characterization of calcium carbonate powder

There are three analyses was performed for the characterization of the calcium carbonate powder which are X-ray Diffraction (XRD, Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscope (SEM)

i. X-ray Diffraction (XRD

X-ray Diffractometer (XRD, PANalytical) model X'Pert PRO that equipped with the 2θ range of 20° to 80° with step size 0.02 was performed.

ii. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR (Perkin Elmer, model Spectrum One) made in USA was used to characterize the functional group and the surface of the nanoparticle. Two scans were performed between the wavenumber 4000 to 515 cm-1 for each spectrum

iii. Scanning Electron Microscope (SEM)

The crystallographic properties of the Precipitate Calcium Carbonate (PCC) was performed using the Scanning Electron Microscope.

III. RESULTS AND DISCUSSION

A. The effects of CO_2 flowrates and Calcium Chloride concentration on the CO_2 hydration

The rate of CO_2 hydration and precipitation of calcium carbonate influence by the flowrate of carbon dioxide gas and the concentration of the calcium chloride. Different CO_2 flowrates and calcium chloride concentration has affect the mass of calcium carbonate precipitate and also the time taken to reach PH 7. The flowrates of 200, 500 and 800 L/min was used while the concentration of calcium chloride was varied from 12.5 g/L, 36 g/L and 48 g/L. The Figure 2 shows the relation between CO_2 flowrate and mass of precipitate $CaCO_3$ formed with present of Carbonic Anhydrase (CA).

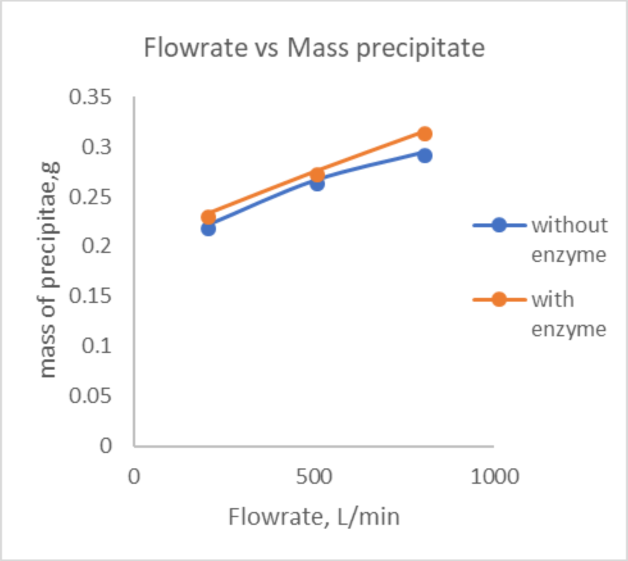


Figure 1: Effect of flowrate on mass precipitate produced

Based on our result, the higher mass of precipitate was obtained at flowrate 800 L/min. From the Figure 2, the mass of the precipitate was increased when the CO_2 flowrates is getting higher. Plus, the mass of the precipitated produced are higher. According to the research by Mahmut Altiner (2018), the increase of CO_2 flowrates produces high amount of $CaCO_3$ precipitate due to the high CO_2 as feedstocks [4]. The formation of calcium carbonate from the carbon dioxide gas was shown by the equation below

Dissolution

$$CO_{2(g)} \leftrightarrow CO_{2(aq)} \quad (1)$$

Carbonic acid reaction

$$CO_{2(aq)} + H_2O \leftrightarrow H_2O_3 \quad (2)$$

Bicarbonate reaction

$$H_2O_3 \leftrightarrow H^+ + HCO_3^- \quad (3)$$

Carbonate reaction

$$HCO_3^- \leftrightarrow H^+ + CO_3^{2-} \quad (4)$$

Calcium carbonate reaction

$$Ca^{2+} + CO_3^{2-} \leftrightarrow CaCO_3 \uparrow \quad (5)$$

First the gaseous carbon dioxide was dissolved in water. In the carbonic acid reaction, the formation of H_2O_3 was known as rate limiting step. The carbonic anhydrase (CA) enzymes was introduced to increase the CO_2 sequestration process by the conversion and mineralization of CO_2 to produce the $CaCO_3$. The carbonic anhydrase is known as zinc containing enzymes which involve in catalyzing the reversible hydration of carbon dioxide. In human body, the CA enzymes is involved with catalyzing inter conversion between carbon dioxide and bicarbonate. The Figure 2 shows the involvement of CA enzymes in CO_2 hydration.

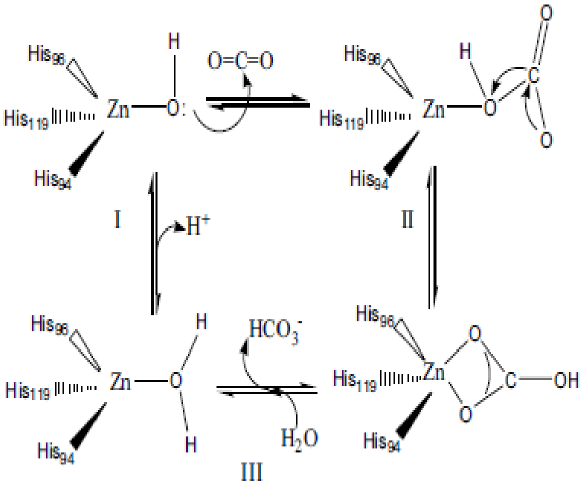


Figure 2: The action of CA enzymes in hydration of CO_2

The CA enzymes has been highlighted as the fastest enzyme which could increased the mass transfer between of the carbon dioxide into aqueous solution. Hence produce the mineral carbonate such as calcium carbonate or magnesium carbonate. The capability of CA enables it to be employed in the carbon dioxide sequestration process. From this situation the higher flowrate of the carbon dioxide gas assists the CO2 to penetrate into the aqueous solution of calcium ions.

Another parameter that been varied in this study is the concentration of the calcium chloride. the Figure 3 shows the plot of calcium chloride concentration versus mass of $CaCO_3$ precipitated formed.

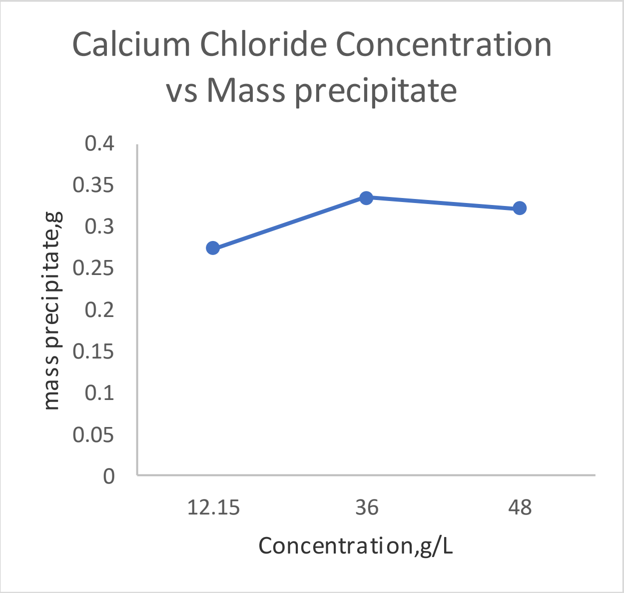


Figure 3: The relation between calcium chloride concentration and mass of precipitate

From the result in Figure 3, it show that when the concentration of calcium chloride was increased, the mass of precipitated obtained was higher. The higher concentration of calcium chloride provide more Ca^{2+} ions which produce high amount of calcium carbonate.

The different CO_2 flowrates and concentration of calcium chloride also effect the time to reach pH7. Form the research conducted by Altiner, the carbonation reaction was stopped at pH 7.5. The reason because, the calcium carbonate precipitate (PCC) particle which dispersed in the carbonate solution was no longer dissolved which caused by the high concentration of HCO_3^-.Besides, at pH 7.5, it can promote the dissolution of calcium carbonate. The time taken for each samples were shown in the Table 1 and Table 2

Table 1: Effect different flowrate and constant temperature

Flowrate (mL/min) at temp 30°C		Time taken to reach pH7
200	w/o run 1	14 min 33s
	w/o run 2	21 min 27s
500	w/o run 1	6 min 50s
	With run 1	6 min 10s
	With run 2	6 min 52s
800	w/o run 1	4 min 31s
	With run 1	4 min 39s
	With run 2	4 min 21s

Table 2: Effect different concentration. Constant flowrate and temperature

Concentration at temp 30°C	run	Time taken to reach pH7
12.15 g/L	w/o run 1	5 min 00s
	w/o run 2	4 min 56s
36 g/L	w/o run 1	4 min 20s
	w/o run 2	4 min 40s
48 g/L	w/o run 1	5 min 18s
	w/o run 2	4 min 28s

B. The analysis of Calcium Carbonate Precipitate

In this research, there were three analysis were performed for characterization of calcium carbonate precipiate which were FTIR, XRD and SEM. The Figure 4 show the FTIR spectrum of the CaCO3 precipitate obtained from the study.

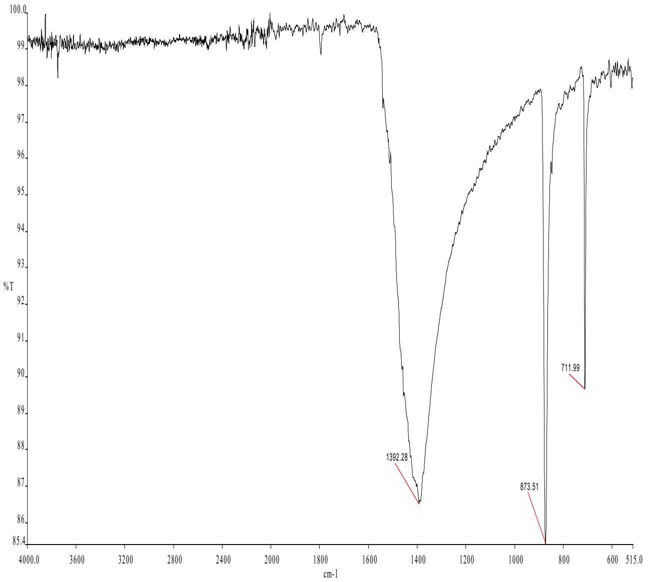


Figure 4:The FTIR analysis or calcium carbonate

Based on FTIR spectrum in Figure 3, the peaks was shown at 1392.28 cm-1, 873.51 cm-1 and 711.99 cm-1. According to the (Jimoh et al., 2017), the typical FTIR spectrum for calcite is around 1433, 874 and 713 cm–1. Thse value is closer to the FTIR spectrum that obtained from analsyis. the position of the peaks can used to detemine the functional group that present in the precipitate. For example, at peak 1392.28 cm-1, the peaks represent the C-O strech. According to the research by (Bao et al., 2015), the asymmetric stretching and bending vibration of CO_3^{2-} occur at absorption peaks at 2514,1423,876 and 712 cm-1. This value was closer to absorption peaks obtained in this research. While Figure 5 shows the results for XRD analysis of calcium carbonate precipitate in our study.

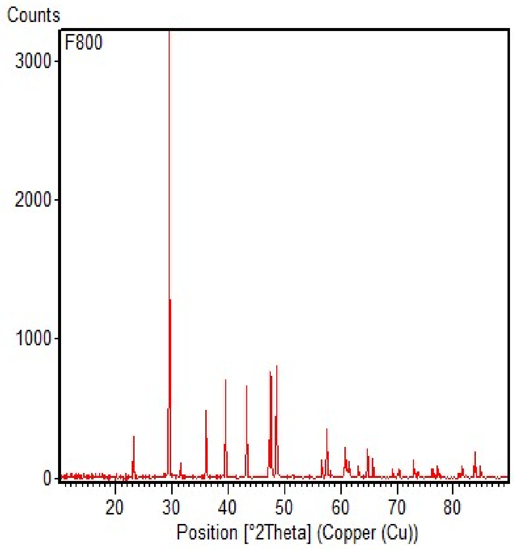


Figure 5: The XRD spectrum for calcium carbonate

Based on the figure 5, the peak produce show a needle peak which indicate that the peak for crystak structure. According to the Daskalakis et al., 2015), the calcite XRD spectrum corresponding to 2 theta was 23.05, 29.40 and 35.96 as shown in the result. Thus, hydration process of carbon dioxide produced calcite phase of calcium carbonate. According the (Kim et al., 2012), there were two forms of calcium carbonate crystal was formed which are calcite and vaterite. Both of the form have own peaks pattern. The calcite have the diffraction peaks at $2\theta = 23.07$, 29.42, 36.0, 39.43, 43.3, 47.53, and 48.53. while diffraction peaks for vaterite was obtained at $2\theta = 24.89$, 27.05, 32.74, and 43.84. According to the (Sharma, Bhattacharya and Shrivastava, 2011), the major form of calcium carbonate that produce through the biomimetic CO2 sequestration was the calcite phase which showed the diffraction peaks at $2\theta = 29.4°$ and 43.8°[13]

For the SEM analysis in the Figure 6, the image show the surface morphology of calcium carbonate. The rectangular shape of the $CaCO_3$ was identified from the image. The FESEM image by (Li et al., 2013) also indentified the most of the $CaCO_3$ crystal formed was crystal which similar to the image obtained through the observation[8]. The research by (López-Periago et al., 2010) has explained the morphology of the calcite which has a rhombohedral crystal structure with {1 0 4} face that indicate as stable suface[10]. The morphology of calcite which smooth surface and consist regular crystal size had make the calcite to been used in the industries.[7].

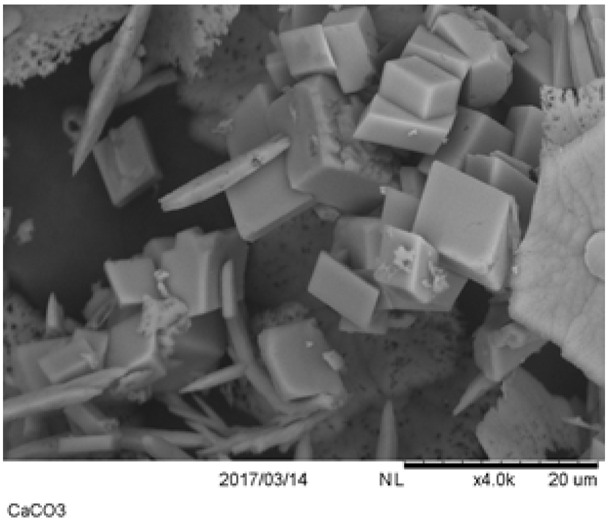


Figure 6: The SEM image for surface morphology of calcium carbonate

IV. CONCLUSION

From the data obtained, the hydration process and precipitation process can be accelerated using the carbonic anhydrase enzyme. The mass precipitate produced and time taken to reach pH 7 was different when the different CO_2 flowrates and concentration of calcium chloride was employed. Hence showed that the CO_2 flowrates and $CaCI_2$ concentration affect the rate of hydration and precipitation process of calcium carbonate. Based on the plot, the higher of CO_2 flowrate will produce higher mass of precipitate. For the effect of the concentration, the higher concentration will produce high amount of calcium carbonate precipitate. However, when the concentration was getting higher the mass precipitate formed was low. From this study, at flowrate 800 L/min, the mass precipitate obtained was the highest. While, for the effect of calcium chloride concentration, the highest of mas precipitate obtained was at 36 g/L. The plot in Figure 3 also revealed at 48 g/L the mass precipitate obtained was low.

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