



# Absorption of Flue Gas Carbon Dioxide in a Wet Scrubber using Sodium and Calcium Hydroxide Solvents

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**Abstract** The release of carbon dioxide gas into the atmosphere is chiefly responsible for increased warming that is in turn causing changes in global climatic patterns. In order to minimize the impact this gas have on the environment, it is necessary that a capturing mechanism be developed. The main objective of this research therefore was to develop a method that would assist in reduction of carbon dioxide emissions generated from fossil fuel based combustion plants. The study also sought to establish the influence of concentration of hydroxide (calcium and sodium) solvents on the absorption of carbon dioxide. Diluted concentration of between 0 to 0.015 mol/liter was studied for two types of solvents namely; sodium hydroxide and calcium hydroxide. The former absorbed more than 14% of carbon dioxide compared to plain water while the latter absorbed more than 35%. The improved performance of calcium hydroxide was attributed to its unique ionization capacity. Higher concentrations in the range between 0.05 and 0.15 mol/liter were also tested for both hydroxides. Sodium hydroxide was found to have superior performance which was attributed to its higher solubility.

**Keywords** absorption rate, carbon capture, fossil fuels, solvent concentration

## 1. Introduction

The increased use of fossil fuel to supply energy in the world has been found to cause emission of carbon dioxide. In 2008, the world total accumulation of carbon dioxide emission from coal, oil and natural gas stood at 30 billion tonnes according to International Energy Agency (IEA) [1]. This has accelerated changes in global conditions such as more prolonged droughts, floods, melting of ice masses in the polar regions and acidification of oceans [2]–[4].

While use of non fossil fuel sources of energy would present the best option to mitigate carbon emission, a rapid shift would disrupt the global economy. Therefore, fossil fuel based sources shall continue to form the main source of energy in the transition period as other sources are sought. Carbon capture is a concept receiving increasing research attention in which carbon dioxide is removed before or after combustion. In the latter method, existing combustion devices such as coal, natural gas or liquid fueled power plants do not undergo major restructuring due to compatibility with capture

systems [5]. Major research efforts are underway to improve the technique and facilitate its capacity to mitigate global warming.

Carbon dioxide forms between 13 to 15% of an exhaust emission stream. According to Anna et al. [6] the most versatile capture technique for such cases is wet scrubbing based on efficiency. Scrubbers rely on diffusion of gas particles to the liquid phase due to a concentration gradient. This diffusion has been found to be influenced by the type of liquid medium used in the absorber. The concentration gradient between the liquid and gas phase govern the degree of absorption. Among the liquid solvents that have been applied in absorption of carbon dioxide as a greenhouse gas are alkanolamines, sodium hydroxide and calcium hydroxide.

Alkanolamines such as monoethanolamine (MEA), diethanolamine (DEA) and methyldiethanolamine (MDEA) have good absorption properties due to high reaction rates with carbon dioxide according to Ardisorn et al. [7]. However, they corrode interior surfaces of absorbers thus reducing the lifespan of the system. Work by Mo-



hammad et al. [8] has shown that applications of alkanolamines should be at low pressures and temperatures to prevent solvent degradation. Finally, the quantity of energy required for the regeneration of carbon dioxide makes them inappropriate for bulk removal of carbon dioxide gas though they have good absorption qualities [9]. However, Derks [10] found that addition of an activator such as piperazine caused reaction properties of alkanolamines to be retained thus reducing the energy consumed during regeneration. Piperazine (PZ) is an alkanolamine that is blended with primary amines (such as monoethanolamine) to reduce overall heat of reaction in the mixture. A phenomena common to alkanolamines is the release of ammonia gas due to their chemical structure which together with high cost continue to limit their application in carbon dioxide absorbers in flue gas systems [11]. This has caused continued search for other solvents.

As a solvent, sodium hydroxide reacts with carbon dioxide and has high solubility in water making it useful in mitigation of carbon dioxide. Among those who have done research using sodium hydroxide are Olutoye et al. [12], [13], who mathematically modeled the absorption of carbon dioxide by the solvent. This work focussed on the amount of time required for reacting species to be consumed but not on influence of variables such as flow rate, temperature and concentration. Higher exposure times increased reaction between gas and solvent which was attributed to increase in diffusion of hydroxide ions. Chia and Chen [14] using a rotating packed bed scrubber also studied the performance of sodium hydroxide in carbon dioxide control. In this work, influence of gas and liquid flow rates as well as concentration of solvent were analyzed. It was observed that an increase in liquid concentration and flow rate enhanced carbon dioxide absorption rate. This occurred in a cross flow rotating packed bed absorber. Increase in gas flow rate was found to reduce absorption due to reduced contact time as flow rate increased. In comparison to ammonia solution, NaOH was found to have higher absorption potential as a solvent [15]. This is a discrepancy considering, that in earlier work by Ardisorn [7], MEA was found to be a more superior solvent to absorption of carbon dioxide compared to NaOH.

Calcium compounds have a capacity to absorb carbon dioxide gas but performance is limited by the solubility. To prove this, Gajda [16] tested carbonate content of fresh and old concrete samples (concrete is a calcium compound) from buildings and found a cumulative increase of carbonate with time. This means that buildings act as atmospheric carbon dioxide sinks, besides the conventionally known sinks such as oceans and forests. Sohbi et al. [17] used a vibrating bubble column absorber to study absorption of carbon dioxide by calcium hydroxide. This was done by varying both vibration frequency and gas flow rate. It was established that high gas flow rates enhanced absorption rate of carbon dioxide.

In this paper the performance of an absorber based on

variation in solvent concentration of liquid medium is presented. This involves comparison of performance of sodium hydroxide and calcium hydroxide in absorption of carbon dioxide. The tests were done using a rig designed to have capacity for control of flow parameters and a brief description of the rig is outlined below.

## 2. Experimental Setup and Method

A packed scrubber was designed and developed for tests on the absorption of carbon dioxide gas. This was based on the procedure used by Schenelle and Brown [18]. The setup shown in Figure 1 was designed to ensure a counterflow interaction between carbon dioxide gas and the scrubbing solvent. The set up of the experiment is shown in Figure 1.

The absorber ensured gas and liquid interaction for mass transfer. Corrugated packed bed, mist eliminator and spray nozzles that facilitated mass transfer in the absorber were installed. The corrugated packed bed shown in Figures 2(a) and 2(b) provided the necessary surface for mass transfer. The height of the packed bed was chosen so as to lie within the recommended range (300 to 1200 mm) to ensure sufficient space for other elements such as spray nozzles and mist eliminator, Figure 3.

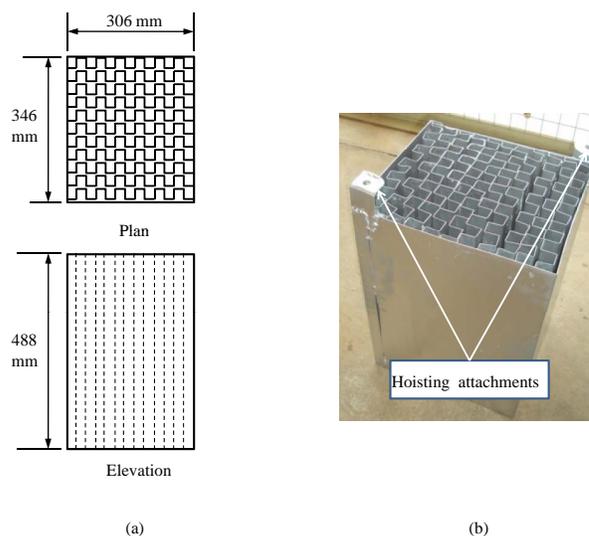


Fig. 2. Packed bed section of the absorber

The performance of the rig was measured by carrying out a balance of molar flow rate of gas, before and after entry to the absorber. The maximum static pressure of gas within the system was found to be 120 mbar, making the plant operate at a low pressure regime. Therefore, the equation of state of a perfect gas was used to determine the molar flow rate of carbon dioxide at the upstream and downstream section of the absorber. By carrying out a balance of molar flow rate at the inlet and outlet of the absorber it was possible to quantify the absorbed carbon dioxide. To accomplish this, properties such as pressure, temperature and volume flow rate changes were

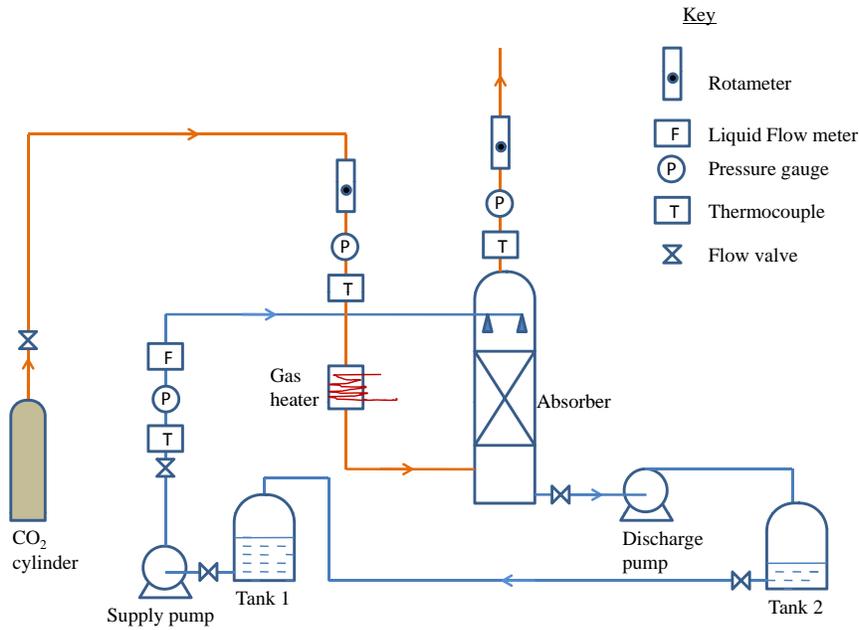


Fig. 1. Layout of the CO<sub>2</sub> absorption plant

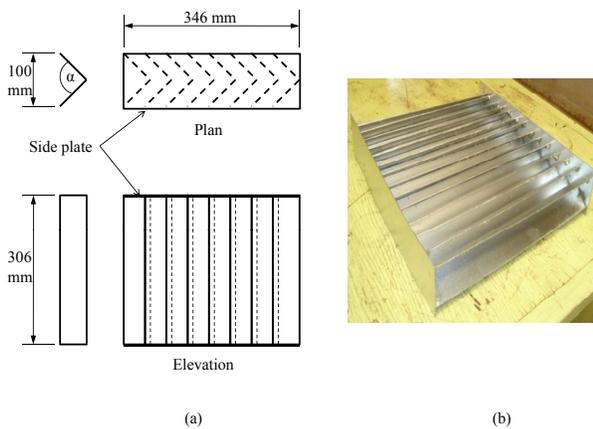


Fig. 3. Interior features of the mist eliminator

measured. This was done using a pair of: rotameters (Model 6G10R3 having an accuracy of  $\pm 5\%$ ), pressure gauges (Cewal type, accuracy of  $\pm 5\%$ ) and thermocouple (J type) connected to an Advantest multichannel digital recorder model TR2724. The solvent pumped to the distribution nozzles at the top of the absorber was monitored using a pressure gauge, thermocouple and a flow meter. A gas drier available in a pressure regulator, Festo LFR-1/2-D MIDI, was installed upstream of the second set of gas measuring instruments to trap any moisture that may have passed the mist eliminator. Further details of the experiment have been described in previous work on performance of wet scrubber by Ndiritu et al. [19].

The criteria of determining the concentration limit of the solvent was based on the solubility of the calcium hydroxide in water. Data available from Amaro et al. [20]

and the Material Safety Data Sheet of calcium hydroxide, [21] suggest that there is a relationship between this solubility and temperature of calcium hydroxide. Indeed solubility reduces with temperature as shown in Figure 4. At a temperature of 60 ° C the solubility of calcium hydroxide in water was approximated by interpolation to be 0.016 mol/liter. Therefore, a limit of 0.015 mol/liter was selected as the maximum solubility for the tests carried out for dilute hydroxides (calcium and sodium). Later, the results of tests of concentrations above 0.015 (ranging between 0.015 and 0.15 mol/liter) are presented for comparison of performance. The molar mass of sodium hydroxide was determined from the sum of individual molar masses of elements forming the compound. Thorough stirring was done upon addition of solute to water to ensure that the obtained solution was homogeneous.

A saturated solution of calcium hydroxide was prepared using the same concentration range of 0.015 and 0.15 mol/liter as in the previous section. The result was a mixture of dissolved solute and a non dissolved solute forming a suspension. The undissolved solute and the solution were at equilibrium such that no more solute can be dissolved at the test temperature. To prevent settling, the suspension is stirred continuously during tests. The solution was stirred for highly concentrated calcium hydroxide because the test period of more than half an hour would cause the undissolved calcium hydroxide to settle at the bottom of the supply tank, thereby affecting solvent flow properties.

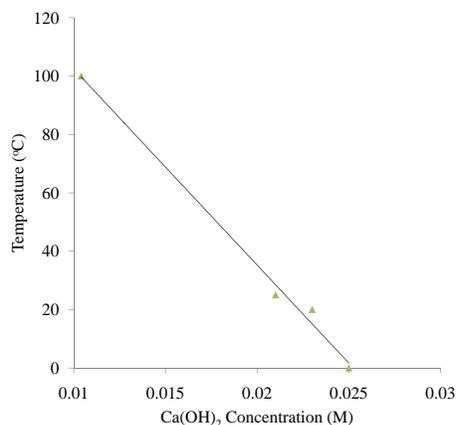


Fig. 4. Heating effect on solubility of calcium hydroxide

### 3. Results and Discussions

The performance of the system was examined and presented in this section are the results of absorption rate of carbon dioxide when varying solvent concentrations were used.

#### 3.1. Uncertainty and Reproducibility

The data obtained from the experimental set up has some level of uncertainty. These are classified as instrumental and experimental uncertainty. Details of these are given in the work by Ndiritu et al. [19]. The performance of the system was measured at the upstream and downstream sections of the absorber. Shown in Table 1 are instrumental uncertainties obtained for gas flow rate, liquid flow rate and solvent concentration. At the upstream and downstream gas measuring sections the uncertainties were found to be below 1%. The absorption rate of carbon dioxide is a difference in molar flow rates at these two sections and this reduced further the overall uncertainty. The uncertainties for the solvent flow rate and concentration were both below 3%. All these values were within the range of accuracies of the instruments used (below 5%).

Table 1. Instrumental uncertainties (%)

Fluid condition	Gas molar flow rate		Liquid flow rate (Volumetric)	Concentration
	Upstream	Downstream		
Uncertainty ξ(%)	0.45	0.51	2.50	2.53

Repeated tests were done to establish the level of reproducibility of the data which is a key element of research. This was based on repeated measurements at a certain condition. Shown in Table 2 are the results of computed uncertainties at selected points.

At these points the uncertainties are less than 5%.

Table 2. Standard deviation of carbon dioxide absorption

Temperature (° C)	Liquid flow rate (liters/min)	Gas flow rate (mol/min)	Standard deviation %
55	1.4	0.4	1.17
55	2.0	0.6	4.72
55	2.0	1.0	3.15

This deviation correspond with the range of accuracy of instrumental uncertainties. Based on these levels of uncertainties the results in the following sections have been obtained.

#### 3.2. Dilute Solution of Sodium Hydroxide

Shown in Figure 5 is the effect of sodium hydroxide concentration on absorption of carbon dioxide in which solvent loading range is from 0.8 to 1.8 liters per minute at a carbon dioxide inlet flow rate of 0.6 mol/min. It is observed that sodium hydroxide absorbs more than 17% of the carbon dioxide that passes through the absorber at a given concentration of solvent. This behaviour is more than 14% compared to that of plain water under the same conditions. This improvement is attributed to increased hydroxide molecules that reacts with carbon dioxide. In addition an interaction occurs resulting to generation of sodium carbonate as shown in Equation 1.

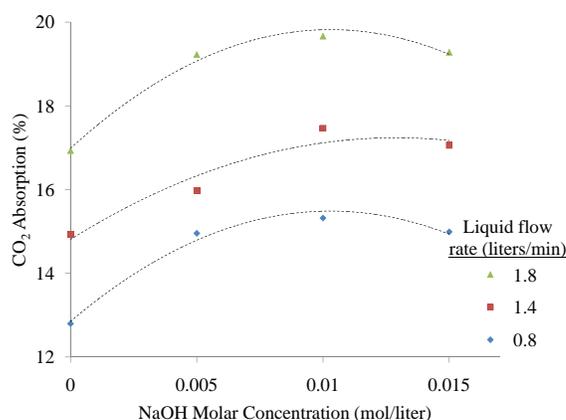
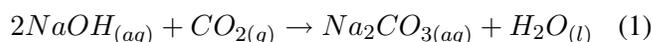


Fig. 5. Carbon dioxide absorption in sodium hydroxide

The observations implies that after interaction with carbon dioxide, the liquid solution contains sodium carbonate in addition to carbonic acid. Confirmation of the proportions of these requires study of kinetics of the reaction.

Chia and Chen [14] studied carbon dioxide-sodium



hydroxide system in a rotating packed scrubber. At a liquid flow rate range of 0.2 to 0.5 liters per minute, increase in concentration was found to cause improvement in absorption of carbon dioxide. This agrees with the results obtained in this research.

### 3.3. Dilute Solution of Calcium Hydroxide

The absorption behaviour when calcium hydroxide solution was used as the solvent is shown in Figure 6. The rig absorbed more than 21% of carbon dioxide passing through it for a given concentration. This quantity is more than 35% compared to that of plain water under similar conditions. This indicates that calcium hydroxide is a better absorber than pure water and the phenomena may be attributed to increased ionization within the solvent causing more hydroxide ions to be released.

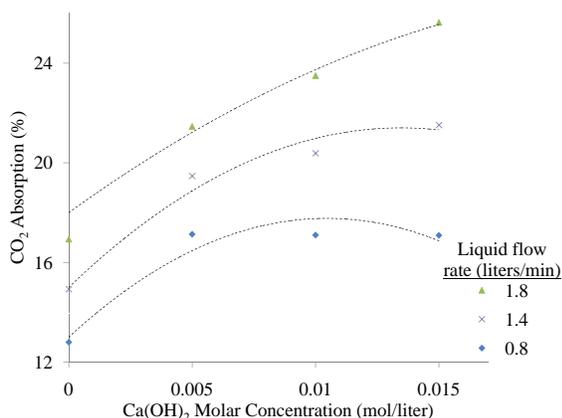
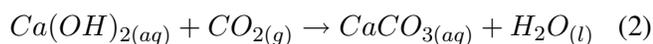


Fig. 6. Carbon dioxide absorption in calcium hydroxide

In addition to carbonic acid formation there is carbonate of calcium formed from the reaction as shown in Equation 2.



Calcium hydroxide thus forms an effective absorbing solution for mitigation of carbon dioxide gas from industrial emissions just like sodium hydroxide and water. Its performance compared to sodium hydroxide is analyzed in the section that follows.

### 3.4. Comparative Absorption

Shown in Figure 7 is the performance of both hydroxides under the same conditions (concentration, liquid and gas flow loading). At a liquid flow rate of 1.4 liters/min, the absorption of carbon dioxide is 57% more for calcium hydroxide compared to sodium hydroxide. This is attributed to higher degree of ionization of the calcium

hydroxide. If a designer of fossil fuel emissions absorber had to make a choice given both dilute hydroxides, calcium hydroxide would be the optimum choice.

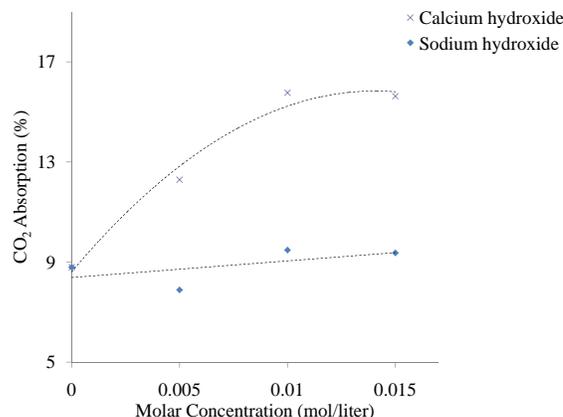


Fig. 7. Comparative absorption in diluted hydroxides

Its unique performance can be traced to the reaction that takes place upon interaction with carbon dioxide as in Equation 2. In this case, one mole of calcium hydroxide is required to form one mole of a carbonate while two moles of sodium hydroxide are required as shown in Equation 1. This means that for the same flow rate of gas and liquid, corresponding concentrations of calcium hydroxide absorb more carbon dioxide.

Locally, the cost of calcium hydroxide is more than twice that of sodium hydroxide which limits its application in large scale emission control in industries. Its absorption capacity is also affected by increase in temperature as shall be observed in the following section.

### 3.5. Absorption of Carbon Dioxide by Concentrated Hydroxides

A higher range of concentration is selected utilizing the high solubility of sodium hydroxide in order to study absorber performance. In this section, results of concentrations in the range between 0.015 and 0.15 mol/liter are selected for both sodium hydroxide and calcium hydroxide are presented. This range affects the solubility of calcium hydroxide, making the resulting mixture a saturated solution.

Shown in Figure 8 is the performance of concentrated sodium hydroxide solution at a gas flow rate of 0.4 mol/min. The solution absorbs more than 39% of carbon dioxide that passes through the absorber at a given concentration and a gas flow rate of 0.4 mol/min. This suggests an improvement of more than twice that exhibited in section 3.2 (for a concentration of 0.015 mol/liter). This is attributed to greater ionization of the solvent and thus



the reaction represented by Equation 1 is more dominant compared to that involving formation of carbonic acid.

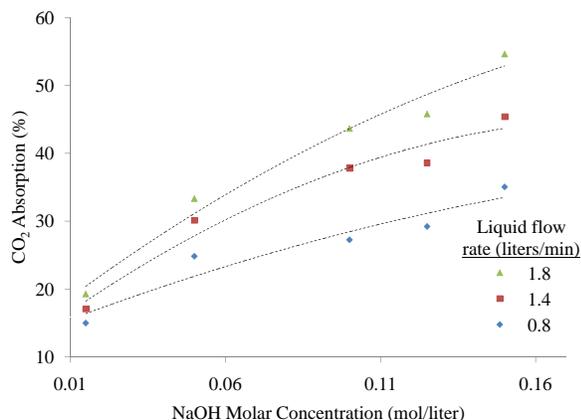


Fig. 8. Absorption in concentrated sodium hydroxide

The performance of calcium hydroxide is shown in Figure 9. The absorption increases by more than 34% compared to the performance when a solvent concentration of 0.015 mol/liter is used in section 3.3. This observation suggests that calcium hydroxide can still absorb carbon dioxide even though it contains particles of undissolved solute. This is attributed to the increased ionization earlier observed in the case of dilute concentrations.

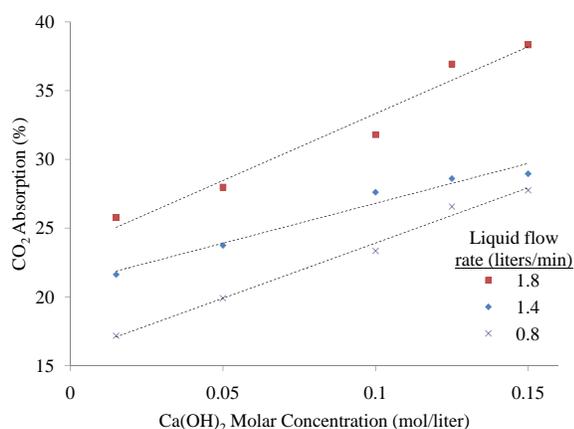


Fig. 9. Absorption in saturated calcium hydroxide

Comparatively the performance of highly concentrated sodium hydroxide is better than calcium hydroxide. Though the absorption of carbon dioxide by calcium hydroxide for dilute concentration (seen in section 3.2) is greater than sodium hydroxide for high concentrations the latter is superior. The significance of this is that the ionization of calcium hydroxide is affected by solubility

with water, thus weakening its performance. Indeed, the undissolved solids reduces its spreading capacity within the absorber making reaction between gas and liquid reduce. The performance of carbon dioxide absorption by undissolved solid calcium hydroxide can be treated as a typical arrangement of adsorption and which is useful in mitigation of carbon dioxide. However further study of this may require a slightly different configuration of equipment.

Based on these observations highly concentrated sodium hydroxide is the best choice among the two hydroxides as a capture medium for industrial use. Further, higher concentrations makes sodium hydroxide overcome the limitations imposed by the reaction mechanism that makes it an inferior solvent for dilute concentrations. Moreover, use of saturated calcium hydroxide presents other challenges that limits its performance. For example, due to continuous stirring of the solution, extra energy is consumed. Further the saturated solution also causes occasional blocking of nozzles as a thick solvent made of undissolved calcium hydroxide flows through them. This observation suggests that use of a saturated solution of calcium hydroxide should only be confined to dilute concentrations for effective absorption of carbon dioxide.

#### 4. Conclusions

Diluted concentration of sodium hydroxide (up to 0.015 mol/liter) causes an absorption of more than 14% compared to tap water. The same range of concentration of calcium hydroxide causes an absorption of more than 35% compared to tap water under similar conditions (gas and liquid flow rates at ambient temperature). This implies that these hydroxides introduce other reactions that facilitate performance of the absorber. The superior performance of calcium hydroxide is attributed to its chemical structure that causes greater ionization compared to that of sodium hydroxide. This further implies that for diluted concentrations (0.005 to 0.015 mol/liter), calcium hydroxide would make the best choice for application in industrial carbon dioxide emission. At ambient temperature this concentration is within the solubility range of calcium hydroxide.

Higher concentrated solutions of sodium hydroxide and calcium hydroxides demonstrates improved absorption of carbon dioxide compared to dilute cases. Concentrated sodium hydroxide absorbs more than twice the quantity of carbon dioxide absorbed under similar conditions when dilute solvents are used. On the other hand a similar concentration of calcium hydroxide absorbs more than 34% of carbon dioxide. This implies that when sodium hydroxide would be the option for absorption of carbon dioxide the best range of concentration would be 0.05 to 0.15 mol/liter. Utilization of concentrations beyond 0.15 mol/liter would be limited by increase in viscosity of the solvent.

It is notable that this work was confined to capture of carbon dioxide gas from the flue gas. Further work



is essential to recover the carbon dioxide gas from the carbonates of calcium and sodium. This may be done by regeneration via heating process. The effect of size and size distribution may also be considered in future work.

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