

## CO<sub>2</sub> Capture through Different Chemical Techniques: A Review

Mushtaq Ahmad Rather<sup>A\*</sup> and Sohail Rasool Lone<sup>A</sup>

<sup>A</sup>Department of Chemical Engineering, National Institute of Technology (NIT), Hazratbal, Srinagar, Kashmir (India)

Accepted 17 December 2013, Available online 22 December 2013, Vol.3, No.5 (December 2013)

### Abstract

Currently 90% of the world's primary energy requirement is supplied by fossil fuels, causing rising emissions of greenhouse gases (GHGs) and related concerns over global warming and climate change. CO<sub>2</sub> is by far the most important of the GHGs, being responsible for about 64% of the enhanced greenhouse effect. As a result of anthropogenic CO<sub>2</sub> emissions, atmospheric concentrations have risen by 30% from pre-industrial levels of 280 ppm to 360 ppm today, primarily as a consequence of fossil-fuel use. In the United States, energy related CO<sub>2</sub> emissions accounted for 98% of the total emissions in 2007 with electricity generation accounting for 40% of the total. This is really alarming and if the trend is continued the rise in the average temperature of globe may go to the extent that glaciers may melt down and sea level will be raised tremendously threatening the very existence of many countries in the world. Above situation demands immediate necessary measures so that biotic life can be kept alive on earth. Greenhouse gas mitigation technologies have assumed growing importance. Carbon dioxide emissions mostly given to rise by the utilization of fossil fuels in various industries and electricity generation can be captured by various techniques. Of these different technologies for CO<sub>2</sub> capture, chemical absorption is the technology that is closest to commercialization now. Lot of research work is being carried out upon this. In India we are also dependent upon the utilization of fossil fuels in our industries and thermal electricity plants. We can no longer ignore the free passage to CO<sub>2</sub> generated in our industries and thermal power plants to atmosphere, when having already witnessed quite recently some environmental catastrophes in form of floods, hurricanes, draughts etc. The CO<sub>2</sub> capturing techniques need to be implemented now practically. Engineers and technologists are for fronted with the challenge of devising such economical techniques. This paper gives a detailed review of CO<sub>2</sub> emission mitigation by utilizing different chemical techniques.

**Keywords:** CO<sub>2</sub>, Capture, Global warming, Absorption

### 1. Introduction

Currently 90% of the world's primary energy requirement is supplied by fossil fuels, causing rising emissions of greenhouse gases (GHGs) and related concerns over global warming and climate change. CO<sub>2</sub> is by far the most important of the GHGs, being responsible for about 64% of the enhanced greenhouse effect. As a result of anthropogenic CO<sub>2</sub> emissions, atmospheric concentrations have risen by 30% from pre-industrial levels of 280 ppm to 360 ppm today, primarily as a consequence of fossil-fuel use. However, at the current state of development and level of risks and cost of non-fossil energy alternatives such as nuclear, biomass, solar energy, etc. these energy sources cannot meet our need for energy as fed by fossil fuels. Additionally, any rapid change to non-fossil energy sources, even if it were, would result in large disruptions to the existing energy supply infrastructure with substantial consequences to the global economy. Some may argue that hydrogen could be a substitute for fossil

energy. But it should be noted that currently most of the hydrogen produced commercially originates from fossil fuels. Per unit of heat generated, more CO<sub>2</sub> is generated by producing H<sub>2</sub> from fossil fuels than by directly burning those fossil fuels. Emission-free H<sub>2</sub> production by water electrolysis, powered by renewable or nuclear resources is as yet not cost-effective (Hoffert et al., 2002). Therefore, the immediate challenge is to reduce CO<sub>2</sub> emissions into the atmosphere, while minimizing any associated negative economic impacts. Thus to meet mid to long term CO<sub>2</sub> reduction targets, cost-effective CO<sub>2</sub> capture from fossil fuels using the different techniques need to be evaluated. Within the mandate of technology road-mapping exercise on CO<sub>2</sub> capture, this paper provides a review of the existing and emerging technology options for the capture of CO<sub>2</sub> from large point source emissions.

### 2. How to capture CO<sub>2</sub>

The objective of CO<sub>2</sub> capture is to produce a concentrated stream of CO<sub>2</sub> which can be transported and sequestered underground or in deep oceans. The CO<sub>2</sub> capture concept

\*Corresponding author: Mushtaq Ahmad Rather

is not new to industry. The capture processes have been widely applied in the natural gas processing and chemical process industries for over 60 years and existing practice is to vent it to atmosphere. The concept of capture for the purpose of sequestration is relatively new. In general, the CO<sub>2</sub> capture can be divided into three categories:

### 2.1 Post-combustion capture

Capture of CO<sub>2</sub> in the downstream of a carbonaceous fuel based combustion unit is referred as post-combustion capture process. Conventional process heaters and industrial utility boilers fit into this category. In these processes, the fossil fuels are combusted in excess air, resulting in a flue gas stream which contains lean compositions of CO<sub>2</sub> (12-15 v/v % for modern coal fired power plants and 4-8 v/v % for natural gas fired plants). In some cases, such as cement kilns and blast furnaces, where flue gases contain process related CO<sub>2</sub> also, the CO<sub>2</sub> concentration in the flue gases may vary from 14-33%. CO<sub>2</sub> from the post combustion flue gases can be captured by numerous techniques such as absorption by amines, membrane separation and cryogenic separation etc. Under the current state of technology, only absorption and to some extent membrane separation technology are considered to be economically viable technologies.

### 2.2 Oxy-fuel combustion

Carbon dioxide capture through oxy-blue combustion capture process. However, removal of nitrogen from the air in the oxidant stream produces highly concentrated flue gas stream (>80 v/v% CO<sub>2</sub>) which can be easily concentrated further through simple gas purification techniques such as cryogenic separations. Although the oxyfuel processes such as RILEE (Recycle Incineration Low Exhaust Emission) process that involves the oxy-fuel burners for treating non-ferrous scrap, have been widely applied, their application in process heaters, in large industrial utility boilers and gas turbines is relatively a new concept and will require comprehensive breakthroughs in terms of low cost oxygen production techniques and combustion in oxygen rich environment.

### 2.3 Pre-combustion capture

The pre-combustion capture process is basically a decarbonization of carbonaceous fuels. In this case, through gasification (controlled oxygen or air) or through steam reforming, the fuel is converted to carbon mono-oxide (CO) and hydrogen. Subsequently, CO is converted to CO<sub>2</sub> through shift conversion resulting in a stream rich in CO<sub>2</sub> and H<sub>2</sub>. The concentration of CO<sub>2</sub> in this stream is around 25-40% and the total pressure is typically in the range of 2.5-5 MPa. Thus, the partial pressure of CO<sub>2</sub> in the pre-combustion capture is very high compared to post-combustion method, making it much easier to separate through techniques such as solvent scrubbing, etc

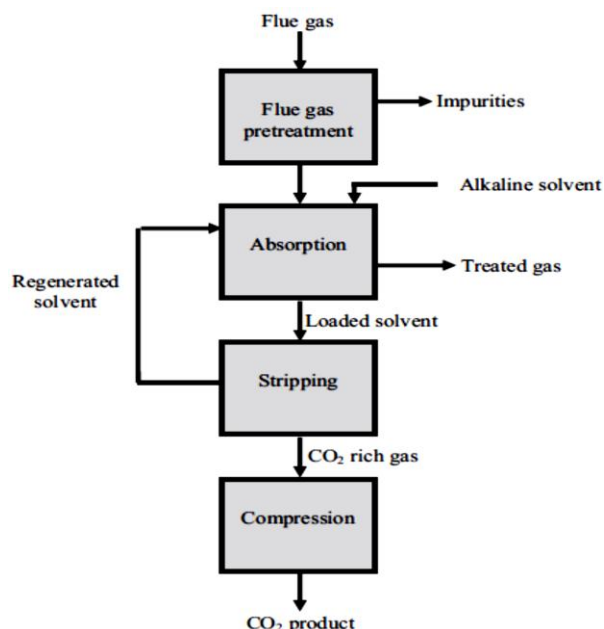
## 3. Different types of CO<sub>2</sub> capture technology

Most CO<sub>2</sub> capture technologies themselves are not new. Specialized chemical solvents were developed more than 60 years ago to remove CO<sub>2</sub> from impure natural gas, and natural gas operations continue to use these solvents today. In addition several power plants and other industrial plants use the same or similar solvents to recover CO<sub>2</sub> from flue gases for application in food processing and chemical industries. The selection of a technology for a given capture application depends on many factors i.e. partial pressure of CO<sub>2</sub> in the gas stream, extent of CO<sub>2</sub> recovery required, sensitivity to impurities, such as acid gases, particulates, purity of desired CO<sub>2</sub> product, capital and operating costs of the process, the cost of additives necessary to overcome fouling and corrosion, where applicable the environmental impacts. Based upon the method of CO<sub>2</sub> removal, capture technologies can be broadly classified into the following categories:

1. Chemical/physical solvent scrubbing
2. Adsorption
3. Cryogenic
4. Membranes

### 3.1 Chemical/physical absorption

Chemical and or physical absorption processes have been widely been used in the petroleum, natural gas and chemical industries for separation of CO<sub>2</sub>. The solvent capacity of an absorbed gas is a function of its partial pressure in the absorption unit. In physical absorption, the solvent capacity or loading, which initially follows Henry's law (for ideal non-interacting gas mixtures), assumes an almost linear dependence on the gas partial pressure. Chemical absorption is the preferred method for capturing CO<sub>2</sub> from post combustion flue gas streams containing low to moderate partial pressures of CO<sub>2</sub> (3-20%). The term absorption here refers to the separation process in which a gaseous component is separated from a gaseous stream by use of a liquid called solvent. The gaseous component basically comes in contact with the liquid and is absorbed from the gas phase to the liquid phase. The liquid that is used for the absorption is often called as solvent or absorbent. These terms are generally used interchangeably. Factors which need to be considered when choosing an absorbent are: (1) the gaseous component solubility in the absorbent and (2) the reactive properties of gaseous component and the absorbent. For example, CO<sub>2</sub> is considered as an acidic gas, which in turn means that when absorbed by water based absorbent an acidic solution will be formed. Thus, for acid gas absorption it is desirable if the absorbent is alkaline. Since alkaline solutions are basic in nature, which enables the neutralization of any acid formed upon the absorption of the gas and hence increasing the absorption of gas which can be absorbed for a given volume of liquid. In the case of CO<sub>2</sub> absorption processes it is common for the flue gas stream to first undergo a pre-treatment step to remove certain impurities such as particulate matter, SO<sub>x</sub> and NO<sub>x</sub>. Figure 2 is the basic flow diagram for post-combustion capture of CO<sub>2</sub> through chemical absorption.



**Fig.1** Basic flow diagram for post-combustion capture of CO<sub>2</sub> through chemical absorption

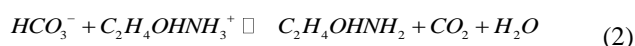
After the pre-treatment step, the gas is cooled and then contacted with the solvent in an absorption column leading to the formation of weak intermediate compounds. After contact with the flue gas, the CO<sub>2</sub> rich solution is then sent to a stripping column, where it is subjected to heating to break down the intermediate compounds. This leads to the regeneration of the solvent and emits a concentrated CO<sub>2</sub> which is then compressed and transported for use. Several chemical absorption processes do exist although differing in the absorbent used to capture CO<sub>2</sub>. The four major processes are: (1) amine absorption, (2) aqua ammonia absorption, (3) dual-alkali absorption, and (4) sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) slurry absorption.

### 3.1.1 Amine absorption

Amine absorption has been in use by the natural gas industry for over 60 years to remove CO<sub>2</sub> from natural gas to produce food and beverage grade CO<sub>2</sub>. Amines are derivatives of ammonia (NH<sub>3</sub>), with one or more of the hydrogen groups with one or more of the hydrogen groups being substituted by a functional group (e.g. ethanol). Amine absorption closely follows the process flow diagram shown in Fig.1. With amine absorption, the flue gas is cooled to 40-60 °C and contacted with the amine solution in a packed absorption column for capture. Some commonly used amines include monoethanol amine (MEA), diethanol amine (DEA) and methyl diethanolamine (MDEA), with the most common being MEA due to its low cost. The chemical reaction between CO<sub>2</sub> and MEA leads to the formation of MEA carbamate and bicarbonate solution. The reaction can be seen in Eq. (1). The weight % MEA in solution can vary from 15-35% depending upon the process.



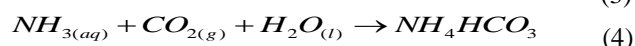
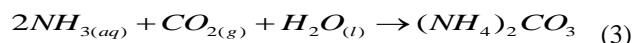
It has been reported that a 35% by weight MEA solution has a CO<sub>2</sub> carrying capacity of 0.40 kg CO<sub>2</sub>/kg MEA in clean flue gas stream (i.e. no impurities are present). If there are impurities such as NO<sub>x</sub> and SO<sub>x</sub> present in the flue gas, they will be absorbed and react with the amine to form heat stable salts (HSS). These heat stable salts can cause plugging in the equipment and drastically reduce the CO<sub>2</sub> capacity of the solvent; hence these impurities are to be minimized. After absorption, the loaded CO<sub>2</sub> solution is sent to a stripping column, where it is heated between 100 °C and 200 °C to produce a gas stream consisting of 99% CO<sub>2</sub> consisting of 99% CO<sub>2</sub> and regenerate the MEA solvent. The CO<sub>2</sub> stream is compressed and transported for geological storage, use in the food and beverage industry, or urea production. The regeneration reaction can be seen in Eq. (2).



The regenerated solvent is cooled to 40-60 °C and passed through a reclaiming stage so as to remove any ammonia and HSS that formed before being recycled back to the absorber unit. The reclaiming unit is used to regenerate the additional MEA solvent by reacting the HSS with caustic at elevated temperatures. The regenerated MEA solvent has a CO<sub>2</sub> carrying capacity of 0.036 kg CO<sub>2</sub>/kg regenerated solution.

### 3.1.2 Aqueous Ammonia Absorption

The aqueous ammonia (NH<sub>3</sub>) process has gained interest, because of the speculation that it could simultaneously remove NO<sub>x</sub> and SO<sub>x</sub> along with CO<sub>2</sub> from flue gases. For absorption with ammonia, the flue gas is first cooled to 15-27 °C (due to the volatile nature of ammonia) and is then contacted with the ammonia solution in a packed bed absorption column to capture CO<sub>2</sub>, and possibly NO<sub>2</sub> and SO<sub>3</sub>. The reaction mechanisms for CO<sub>2</sub> capture in an ammonia solution are as:



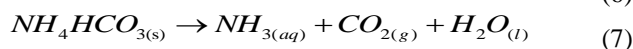
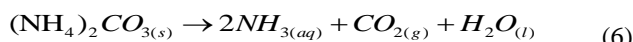
Possible products that are formed during CO<sub>2</sub> capture using aqueous ammonia include solid ammonium carbonate and bicarbonate. Bai and Yeh reported the formation of solid NH<sub>4</sub>HCO<sub>3</sub> upon sparging CO<sub>2</sub> through an ammonia solution. They also that a 35 wt% ammonia solution has a carrying capacity of 1.20 kg CO<sub>2</sub>/kg NH<sub>3</sub> in a clean gas stream. If the impurities NO<sub>x</sub> and SO<sub>x</sub> are also present in the flue gas, it may be advantageous to simultaneously capture them along with CO<sub>2</sub> using the same solution. For simultaneous capture of SO<sub>x</sub> and NO<sub>x</sub>, pretreatment requires an oxidation stage in which the NO<sub>x</sub> and SO<sub>x</sub> are oxidized to NO<sub>2</sub> and SO<sub>3</sub>. This step is needed, because ammonia solutions can only absorb NO<sub>2</sub> and SO<sub>3</sub>

forms of  $\text{NO}_x$  and  $\text{SO}_x$  gases. Equation (5) shows the reaction between ammonia solution,  $\text{NO}_2$  and  $\text{SO}_3$ .



It can be observed from the above reaction that solid ammonium nitrate and sulfate will be formed upon reaction with the ammonia solution. This is advantageous, because both are well known fertilizers which could possibly be sold to generate revenue.

After the capture of  $\text{CO}_2$ , the  $\text{CO}_2$  loaded solution is then sent to a stripping column, where it is heated between 27 and 92 °C. The ammonium bicarbonate and carbonate thermally decompose at these temperatures releasing  $\text{CO}_2$  and regeneration the original ammonia solvent. The  $\text{CO}_2$  stream is compressed and then transported for geological storage, use in the food and beverage industry, or urea production. The regeneration mechanisms can be seen in Eqs. (6) and (7).

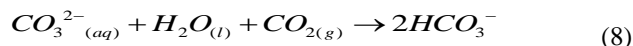


After stripping the regenerated ammonia solution has a  $\text{CO}_2$  carrying capacity of 0.07 kg  $\text{CO}_2$ /kg solution. This loss in carrying capacity is attributed to heavy  $\text{NH}_3$  losses in the vapor stream during stripping.

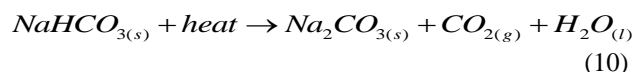
### 3.1.3 Absorption with sodium carbonate slurry

Using  $\text{Na}_2\text{CO}_3$  solutions,  $\text{CO}_2$  was captured in early 1900s for the production of dry ice. A computer simulation has been conducted by Knuutila and coworkers to examine using a  $\text{Na}_2\text{CO}_3$  slurry to capture  $\text{CO}_2$ . All data that will be discussed in this section have been obtained by computer simulation using CHEMCAD 5.6. The simulations varied the  $\text{Na}_2\text{CO}_3$  wt% (10-30%), the inlet liquid temperature (45-70 °C), inlet flue gas temperature (45-70 °C), liquid to gas (L/G) ratio (2.1-5.5) and the stripper pressure (1-2 bar) to determine the optimal  $\text{CO}_2$  capture efficiency and amount of energy required to operate the stripper. Optimal conditions determined by the simulation were: 30 wt%  $\text{Na}_2\text{CO}_3$  slurry, inlet liquid temperature of 60 °C, inlet flue gas temperature of 70 °C, L/G ratio of 2.3, and stripper pressure of 2 bar. At these conditions, the simulation predicted 90%  $\text{CO}_2$  capture efficiency and an energy requirement of 3.2 MJ/kg  $\text{CO}_2$  in the stripper. For running the simulation, a sulphur free flue gas was assumed.

As previously mentioned, for the capture of  $\text{CO}_2$  it was found through the simulations that a 30 wt%  $\text{Na}_2\text{CO}_3$  slurry and an inlet flue gas temperature of 70 °C was optimal. This creates an environment in which  $\text{NaHCO}_3$  precipitates out of solution allowing for more  $\text{Na}_2\text{CO}_3$  to dissolve in solution, thereby leading to an increase in the  $\text{CO}_2$  carrying capacity of the solution. The capture of  $\text{CO}_2$  and precipitation of  $\text{NaHCO}_3$  via the carbonate slurry can be seen in Eqs.(8) and (9).



There was no mention made to the  $\text{CO}_2$  carrying capacity of the slurry in the study performed by Knuutila and coworkers. However, a quick calculation based on Eq. (20) gives a theoretical carrying capacity of 0.73 kg  $\text{CO}_2$ /kg  $\text{CO}_3^{2-}$ , which is higher than that of MEA (0.40 kg  $\text{CO}_2$ /kg MEA). Because of the presence of impurities, the carrying capacity is likely to decrease. For example, if the flue gas contains  $\text{SO}_2$ , it may be absorbed by the solution, most likely creating sodium sulfite ( $\text{Na}_2\text{SO}_3$ ) and sodium bisulfate ( $\text{NaHSO}_3$ ) in solution. This would lower the carrying capacity of the  $\text{Na}_2\text{CO}_3$  slurry, but provides multi-pollutant control system. Pre-treatment of the flue gas would also be optional when using a  $\text{Na}_2\text{CO}_3$  slurry. The  $\text{CO}_2$  slurry is sent to a stripping column where it is heated to 121 °C at a pressure of 2 bar to drive off  $\text{CO}_2$  and produce solid  $\text{Na}_2\text{CO}_3$ . The mechanism can be seen in Eq.(10).



## 4. Indian Perspective

Economic growth in India has led to a rise in energy demand, which in turn has led to an increase in overall  $\text{CO}_2$  emissions, as the vast majority of its energy has been supplied by fossil fuels. More than 70% of India's carbon emissions come from burning fossil fuels, a significant proportion of them from coal-fired power plants. Coal is the most  $\text{CO}_2$ -intensive of all fossil fuels and it is responsible for more than 50% of historical emissions. Many countries, including India are planning to build coal-fired power plants, the lifespan of which means they will be emitting  $\text{CO}_2$  at a time when emissions must be reduced in the power sector worldwide to prevent dangerous climate change. Carbon capture refers to the processes that capture  $\text{CO}_2$  from the emissions produced by fossil fuels (coal,oil,gas) burning power stations. While this is a relatively immature technology, that has yet to be tested on a commercial-scale power plant, it is already being promoted very widely as part of a solution to climate change.

India has yet to be convinced that it has the responsibility or the capacity to adopt CCS (Carbon Capture and Storage) as part of the global fight against climate change. This may be due to technical uncertainties about CCS technology, particularly to suit Indian conditions; concerns about lack of a geological storage capacity in India and the cost of financing the construction and the ongoing cost of capturing and storing carbon. Although the Indian Government has started considering certain CCS projects for potential applications for support under the Clean Development Mechanism (CDM), including one that plans to use  $\text{CO}_2$  from an offshore sour gas facility at Hazira, Gujarat for enhanced oil recovery (EOR) at an onshore site 70 km away. There has, however,

been dispute around whether CCS projects should be included in the CDM.

India needs assurances from the international community before it will risk adopting new carbon capture technologies. The cost of CCS is currently viewed as prohibitively high. The opportunity cost of developing coal with CCS must also be recognized. The more resources devoted to CCS, the bigger the sacrifice of fully renewable technologies, such as concentrated solar power and wind power. To make CCS more attractive to India, there will have to be sufficient, reliable, long-term finance available from the industrialized world. It is needed now to encourage new power stations to be carbon-capture ready and in future to pay for the installation of CCS technology and compensate for the resulting increase in the cost of power generation.

## 5. Conclusions

Post combustion capture technologies possess the greatest potential for near term implementation at the level of fossil-fuel fired power plants, because they can be retrofit to the existing facilities with the least difficulty. Of the current post-combustion capture technologies, chemical absorption with amines is the most mature technology.

## Acknowledgment

This work was supported by The National Institute of Technology, Hazratbal, Srinagar, Kashmir (India)

## References

- M. Gupta, I. Coyle & K. Thambimuthu (Sept 2003), CO<sub>2</sub> Capture Technologies and Opportunities in Canada, CANMET Energy Technology Centre, Natural Resources Canada, 1<sup>st</sup> Canadian CC&S Technology Roadmap Workshop, 18-19, Calgary, Alberta, Canada.
- Brett P. Spigarelli & S. Komar Kawatra (2013), Opportunities and Challenges in Carbon dioxide Capture, *Journal of CO<sub>2</sub> Utilization*, 69-87(1).
- M. Wang et al (2011), Post-combustion CO<sub>2</sub> capture with chemical absorption: A state of the art review, *Chemical Engineering Research and Design*, 1609-1624(89).
- J.C.M. Pires et al (2011), Recent developments on carbon capture and storage: An overview, *Chemical Engineering Research and Design*, 1446-1460(89).
- M. Goel Carbon Capture and Storage Technology for Sustainable Energy, Centre for Studies in Science Policy, Jawaharlal Nehru University, New Delhi, India.
- R.V. Kapila et al, Investigating the prospects for Carbon Capture and Storage technology in India, *School of Geosciences, University of Edinburgh*.
- J.T. Yeh, K.P. Resnik, K. Rygle, H.W. Pennline (2005), Fuel Process. *Technol.* 86 (14-15)
- C.S. Comstock, B.F. Dodge (1937), *Ind. Eng. Chem.* 29 (5), 520-529.
- H.E. Howe, *Ind. Eng. Chem.* 20 (10) (1928) 1091-1094.
- Jose D. Figueroa et al (2008), Advances in CO<sub>2</sub> capture technology- The U.S. Department of Energy's Carbon Sequestration Program, *International Journal of Greenhouse Gas Control*, 2(9-20).