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Carbon Capture and Sequestration: An Overview

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Abstract: Carbon dioxide capture and sequestration (CCS) is the capture and storage of carbon dioxide (CO_2) that is emitted to the atmosphere as a result of combustion process. Presently majority of efforts focus on the removal of carbon dioxide directly from industrial plants and thereby storing it in geological reservoirs. The principle is to achieve a carbon neutral budget if not carbon negative, and thereby mitigate global climate change. Currently, fossil fuels are the predominant source of the global energy generation and the trend will continue for the rest of the century. Fossil fuels supply over 63% of all primary energy; the rest is contributed by nuclear, hydro-electricity and renewable energy. Although research and investments are being targeted to increase the percentage of renewable energy and foster conservation and efficiency improvements of fossil-fuel usage, development of CCS technology is the most important tool likely to play a pivotal role in addressing this crisis. [1]

Keywords: Carbon Capture and Storage, Carbon dioxide, fossil fuels, Greenhouse gases

I. INTRODUCTION

Greenhouse effect is the major contributor to the rising global average temperature. The main cause of increasing global warming is the reliance on fossil fuels for primary energy supply. In India, coal currently contributes around 60% to electricity generation. Furthermore, it is reported that coal will continue to be a major contributor of power generation in India for the upcoming few decades. Efforts on several fronts are being carried out to tackle CO_2 build up in the atmosphere to limit the global average temperature rise to 2°C . Carbon dioxide capture and sequestration (CCS) is seen as one of the most promising options to mitigate CO_2 emissions from large point sources. CCS involves capture of CO_2 emitted from combustion of fossil fuel and kept isolated from the atmosphere for a long period of time.

The three different steps involved in CCS process are- CO_2 Capture, Transport & Sequestration. In the capture step, removal, purification and compression of CO_2 separated from the flue gas takes place. The captured and compressed CO_2 is then transported to the geological sinks. A typical break down of a CCS system into its component parts can be as follows -

- 1) *Capture:* In this method, CO_2 is separated from the effluent and compressed to a liquid state. This results in higher concentrations of CO_2 (>99%), though lower concentrations are also acceptable. Capture is necessary to transport and store the CO_2 economically.
- 2) *Transport:* Transferring CO_2 from the source to the storage reservoir. Transport by truck, train, and ship are all possible, but transporting large quantities is done in the most economical manner by a pipeline.
- 3) *Injection:* Depositing CO_2 into the storage reservoir. The main focus of this paper are geological formations called storage reservoirs. Other potential reservoirs include the deep saline formations, depleted oil and gas reservoirs, and coal seams. [2]

II. CO_2 CAPTURE TECHNOLOGY

There are four basic approaches to capture CO_2 from process streams, which are as follows:

- 1) Separation with chemical/physical solvents (absorption)
- 2) Adsorption
- 3) Separation with membranes
- 4) Cryogenic separation.

The technologies of adsorption and separation by membranes/ cryogenic methods are under development. Only the absorption technology which utilizes chemical or physical solvents to separate CO_2 is available for commercial use. This method consists of two types-

A. Chemical Solvent Scrubbing

In this method, CO_2 is captured from low pressure, concentrated flue gases. The majority of chemical solvents are amine based and Mono-ethanolamine (MEA). Since CO_2 is acidic, alkaline solvents like MEA bond chemically with it. Once the CO_2 has been absorbed by the flue gas, heat can be applied to the absorbent to release the CO_2 for storage while simultaneously regenerating the solvent for reuse in the process.

The flue gas is first cleaned of particulates or other impurities. Then in the absorption vessel, it is brought into contact with the absorbent at temperatures of between 40°C and 60°C allowing CO₂ to react with the solvent and form an intermediate compound. The CO₂ 'rich' solvent is then fed into the top of the stripper column, via a heat exchanger, and heat is applied (100-140°C) to remove the chemically bound CO₂ from the solvent. This produces a CO₂ stream and regenerates the original solvent. Typical CO₂ recovery is between 80-95% with a product purity in excess of 99%. [3]

The disadvantages of using MEA and other amine solvents are:

- 1) A low carbon dioxide loading capacity - 0.4 kgCO₂/kg MEA
- 2) High energy consumption during absorbent regeneration
- 3) A high equipment corrosion rate, which can be prevented using additives.
- 4) High solvent degradation rates in the presence of a range of flue gas constituents including SO₂, NO₂ and O₂.
- 5) Removal and disposal or regeneration of solid salts formed when the MEA combines with SO₂ or NO₂.
- 6) Consumption of activated carbon used for removal of degradation products to prevent the acceleration of the solvent degradation processes – typically around 0.075 kg activated carbon per ton CO₂.

To improve the performance, sterically hindered amines have been developed which require less energy for absorption and regeneration and have higher CO₂ loading capacity than MEA. To improve the performance, other chemicals can be added to amines. Inorganic alternatives to amine-based scrubbers are also commercially available including the use of potassium carbonate combined with a promoter. [4]

B. Physical Solvent Scrubbing

During physical solvent scrubbing, CO₂ from a gas stream is weakly absorbed by the solvent under conditions of high pressure and released when the pressure is reduced to allow solvent regeneration. Selexol is the most used physical solvent. Alternatives include cold methanol (Rectisol), N-methyl-2-pyrrolidone (Purisol) and propylene carbonate. The physical solvents have a lower affinity for NO₂ and O₂. However, SO₂ is readily absorbed and must be removed from a gas stream prior to physical solvent use. Physical solvent scrubbing is best applied to pressurised gas streams containing high concentrations of CO₂ and is generally not considered suitable for post-combustion capture. They are better suited for application at an Integrated Gasification Combined Cycle (IGCC) pre-combustion capture plant where the flue gases contain CO₂ concentrations of 35-40% and are at high pressures. [5]

III. CAPTURE PROCESSES

CO₂ capture processes falls mainly into three general categories:

A. Post-Combustion Capture

Post-combustion capture is a form of flue-gas clean-up. The process is added to the back end of the power plant, after the other pollutant control systems. All commercial post-combustion capture plants use the chemical absorption processes with MEA based solvents. Due to the degradation and corrosion, solvent strength is kept relatively low, which results in large equipment sizes and solvent regeneration costs. MEA only absorbs the CO₂. The CO₂-rich MEA solution is sent to a stripper and heated to release CO₂. MEA solution is then recycled. [6]

B. Oxy-Combustion Capture

Since nitrogen is the major component of flue gas in power plants that burn coal in air, post-combustion capture is essentially a nitrogen-carbon dioxide separation. Thus, after eliminating nitrogen, CO₂ capture from flue gas becomes very simple. In oxy capture, instead of air, oxygen is fed to the plant that is produced on site in an air separation plant. The resulting flue gas is mostly CO₂ and H₂O, which is easily separable.

The primary separation process here is of oxygen from nitrogen. This is done in a standard air separation unit (ASU), but it has a large load of about 15 per cent of a power plant's electric output. Once water is separated, the flue gas is 90 per cent CO₂. However, impurities like SO₂, NO_x and non-condensable oxygen and nitrogen are still present in the effluent. These impurities need to be separated before the CO₂ is sent for transport and injection. [7]

C. Pre-Combustion Capture

Pre-combustion capture is usually incorporated in IGCC power plants. This process includes gasifying the coal to produce a synthetic gas composed of carbon monoxide (CO) and hydrogen (H₂); reacting the CO₂ with water (in a water-gas shift reaction) to produce CO₂ and H₂, then capturing the CO₂ and finally sending the H₂ to a turbine to produce electricity. The primary fuel hydrogen is sent to the gas turbine.

Capturing CO₂ before combustion has some advantages. Firstly, CO₂ is not diluted by the combustion air. Secondly, the CO₂-containing stream is at elevated pressure. Thus, more efficient methods viz. pressure-swing absorption using physical solvents (like methanol or polyethylene glycol) can be applied. However, this method is not much favoured as generation of electricity is much cheaper in PC power plants compared to IGCC power plants. When natural gas is the primary fuel, then pre-combustion process is preferable. The natural gas will react with steam to produce CO₂ and H₂O.

However, in the case of natural gas, it is still not clear, whether pre-combustion capture is better than the standard post-combustion capture. [8]

IV. STORAGE OF CO₂

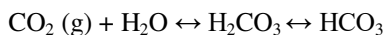
A. Underground Storage

Geological formations in the subsurface are formed by deposition of rock grains, organic material and minerals under the rocks. Generally, water occupies the space between the grains with minute traces of gas and oil. The cavities are also filled with fluid. When injected into the cavities, the CO₂ displaces the already present fluid in the fractures. Sometimes CO₂ gets dissolved or mixed with the in-situ fluid or with minerals or both.

Injection of CO₂ into the pore space and cavities of a permeable formation can displace the in-situ fluid or the CO₂ gets dissolved or mixed with the fluid or reacts with the mineral grains or there may be a combination of all these processes. The most effective sites for carbon storage are where CO₂ is trapped in the seal or it gets absorbed on the coal micropores or gets converted to minerals. This is possible due to the combination of chemical and physical trapping mechanisms. [9]

- 1) *Physical trapping*: Physical trapping of CO₂ is principally the best means to store CO₂ in geological formations due to the low-permeability of seals. Shallow gas hydrates may act as a seal in high latitude areas. Usually, gas, oil and saline water occupy the sedimentary basins which are closed and act as physical traps. Faults can act as both permeability barriers and as pathways for fluid flow. The stratigraphic traps are formed by changes in rock type due to variation in the setting where the rocks were deposited. Both of these types of traps are suitable for CO₂ storage, although, fracturing might occur if the pressure is over-exceeded. Since CO₂ is lighter in nature, it replaces the saline water in the formation after CO₂ is injected. This CO₂ migrates as a separate phase as it reaches the top of the formation. The CO₂ might take millions of years to dissolve in groundwater and reach the surface from deep basins. [10]
- 2) *Geochemical Trapping*: The geochemical trapping mechanisms improve the efficiency and capacity of this process. In the subsurface, CO₂ undergoes various chemical reactions with rocks and minerals and remains underground for a long time. The first step in this process is solubility trapping, where in CO₂ dissolves in water and does not exist as a gas, which prevents its escape. This might be followed by formation of ions due to the dissolution of rocks. Some percent gets converted into minerals, called mineral trapping. This is the most permanent form of storing CO₂ geochemically. However, it is a very slow process and may take more than million years. But it is a desirable form of storage due to the large capacity of storage as well as its sustainability.

Dissolution of CO₂ in formation waters can be represented by the following chemical reaction:



CO₂ flow and transport processes

Fluid is injected deep into these geological storages sites by pumping the fluid into a well. The storage well is perforated to allow the CO₂ to enter the formation. The perforation is usually of 10–100 m thickness, depending on the permeability and thickness of the formation. The pressure caused by the injection drives the CO₂ to displace the fluid already present in the formations. The rate of injection, permeability, thickness and the permeability of the formation ultimately determines the amount of pressure of the injection. [11]

B. Enhanced Oil Recovery

By injecting CO₂, oil recovery can be enhanced, this will lead to economic gains by increasing oil production. About 5–40% of the original oil can be recovered by traditional methods of primary production. Secondary recovery of 10-20% can be achieved by water flooding. If miscible agents like CO₂ are used, this can improve the recovery further up to 7-23%.

Either continuous CO₂ injection or alternating injections of water and CO₂ gas can be used. Oil displacement by CO₂ injection will depend on temperature, pressure and composition of crude oil mixture in the reservoir. Different mechanisms are used to displace the miscible liquid at high pressure, e.g., injecting immiscible fluids at low pressures leading to viscosity reduction and oil swelling. Almost half of the CO₂ is recovered as it is ejected back with oil, this is separated and injected again to lower the costs of the operations. The remaining CO₂ is left trapped, mixed with the reservoir oil.

To improve storage of CO₂ in these operations, there are certain criteria which should be fulfilled by oil reservoirs., e.g., the minimum depth should be 600 m. For heavy viscosity oils, injection of immiscible fluids is sufficient. However, miscible flooding is desirable for light, low-viscosity oils. For miscible flooding, the reservoir pressure must exceed the minimum miscibility pressure. Several factors interact to determine the miscibility between oil and CO₂, e.g., oil composition, gravity, reservoir temperature and CO₂ purity.

Flooding for effective removal of oil from thin reservoirs (i.e., less than 20 m), can be achieved with high reservoir angle, homogenous formation and less vertical permeability. There should be no natural water flow, major gas cap or natural fractures for these horizontal reservoirs. If the reservoir is very homogenous and has high permeability, the lighter CO₂ moves along the top of the reservoir, due to density difference with oil and water. Thus, this will lead to poor CO₂ storage and oil recovery will be affected. Conversely, reservoir heterogeneity has a favourable impact as it decreases the rise of CO₂ to the top of the reservoir. This forces it to spread laterally, allowing better penetration of the formation resulting in greater storage. However, CO₂ storage efficiency is not affected by reservoir thickness and permeability. [12]

V. OCEAN STORAGE

A. Injection Methods

At normal pressure and temperature, carbon dioxide remains in gaseous state, however it converts to liquid form below the depth of 500 m. CO₂ hydrates can be formed below 400m, depending on the compositions of CO₂ and H₂O. This liquid form is more compressible compared to sea-water. It rises till the depth of approximately 3000 m, but becomes negatively buoyant after the depth of 3700 m.

The rising droplet plume has been the one of the easiest schemes to implement. It would rely on commercially available technology to inject the CO₂ as a stream of buoyant droplets from a bottom manifold. Effective sequestration can be achieved by locating the manifold below the thermo line, and dilution can be increased by increasing the manifold length. To achieve better dilution CO₂ is released in droplets from a moving ship which provides additional dispersal. The plumes resulting from these two options would be similar, even though from different sources, each creating a vertical band of CO₂-enriched seawater over a prescribed horizontal region.

Other alternative is by storing carbon in the form of hydrates by reacting CO₂ with seawater under controlled conditions. It is practically impossible to achieve reaction efficiency of 100%, but lab as well as field experiments have shown that even 25% reaction efficiency is sufficient to achieve sinking, i.e., negative buoyancy. The hydrate reactor can be either mobile, e.g., towed by a sailing ship; or fixed to a platform. The seawater density increases due to dissolution of hydrates and together with higher concentration of dense particles, a sinking plume is generated.

The concept of a CO₂ Lake is based on a desire to minimize leakage to the atmosphere and exposure to biota. This requires more expensive and advanced technology, as minimum depth of the lake required will be 3000m, well beyond the depths at which the current off shore industry can manage.

In the lake, CO₂ would be partially in the form of solid hydrates, reducing the dissolution of CO₂ into the water column, thereby also slowing its leakage to the atmosphere. Thus, various technologies can be utilized to physically contain CO₂ on the seafloor, separating it from the water column above it, though they will require additional cost. An alternative method involves forming a sinking bottom gravity current by injection of CO₂-seawater mixture at a depth of 500–1000 m.

Though CO₂-seawater mixture is less than 1% heavier than seawater, this is enough to propagate a sinking density current. But this approach may in fact have more deleterious environmental consequences in view of the concentrated nature of the plume and its contact with the seafloor, especially if the currents are generated by a submarine. [13]

B. CO₂ storage by dissolution of carbonate minerals

Over thousands of years, increased sea water acidity resulting from CO₂ addition will be largely neutralized by the slow natural dissolution of carbonate minerals in sea-floor sediment and on land. Due to the neutralization the ocean absorbs more CO₂ from the air with minimal pH change, pCO₂ and carbonate ion concentration. Various approaches have been proposed to accelerate carbonate neutralization, and thereby store CO₂ in the oceans by promoting the dissolution of carbonate minerals. These approaches do not entail initial separate CO₂ capture and transport steps. However, no tests of these approaches have yet been performed at sea, so inferences about enhanced ocean CO₂ storage and effects on ocean pH are based on laboratory experiments. Carbonate neutralization approaches attempt to promote reaction in which limestone reacts with carbon dioxide and water to form calcium and bicarbonate ions in solution. In that approach, CO₂ is stored by reacting it with non-carbonate minerals to form carbonate minerals. Carbonate minerals are dissolved in the ocean, thereby increasing ocean alkalinity and increasing ocean storage of CO₂. This approach could also make use of noncarbonated minerals, if their dissolution would increase ocean alkalinity. Eventually in about 6000 years, the CaCO₃ dissolution in sea water will decrease limiting the ocean storage. [14]

VI. CONCLUSION

In this report we studied an assessment of CO₂ capture and storage as an option for the mitigation of climate change. Capturing carbon is the first and very important step to generate a condensed stream that can be easily stored. The main natural reservoirs which could hold CO₂ are geological formations and the deep ocean; considers the geographical correspondence of CO₂ sources and potential storage reservoirs. CO₂ capture and storage are most applicable to large, centralized sources like power plants and large industries. This technology can enable us to have a scope of carbon neutral balance in the atmosphere, allowing electricity production with minimal carbon emissions. The limitations of the present process are that the energy to operate this system and waste produced are much more than the conventional plants. In the future more efficient plants would be required to make the net impact zero. The top priorities in the development for CCS technology would be to minimize the costs and environmental impacts, also increase the capture efficiency. Various technologies have been devised increase ocean CO₂ storage. The CO₂ can be transported via ship and can be injected directly in the ocean. CO₂ loaded on ships could either be dispersed from a pipe or transported to fixed platforms feeding a CO₂ lake on the sea floor. Such CO₂ lakes must be deeper than 3 km where CO₂ is denser than sea water. [15]

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