1

INTRODUCTION

The Industrial Revolution has not only changed the way people live, but also the behavior of the earth and the atmosphere that surrounds it. Huge advances have been made in the mechanization of agriculture, manufacturing, mining and transportation - but at a cost. Behind the machinery is steam power and behind the steam is coal and we burn it in huge quantities. The climate change the planet experiencing in recent years is due to the escalating levels of carbon emissions coming predominantly from our continued use of fossil fuels. These anthropogenic activities may lead to disastrous consequences endangering the survival of life on the earth. It is now believed that anthropogenic CO_2 is the most significant green house gas (GHG) contributing to more than 50% to the global warming and climate change.

At present 88% of the world's energy needs are faced only with fossil fuels and will remain the world's overriding source of energy over the next several decades constantly adding to global greenhouse gas emissions. On a global level, approximately 31 billion tonnes of CO_2 are emitted per year into the atmosphere. According to the chart, there are 1811 large stationary sources in the United States which are emitting more than 100,000 tonnes of CO_2 per year and in Canada it is about 219 sources. Power plants account by means of the largest share of emissions from stationary sources (80% in the US,45% in Canada) but other big emitters include the oil and gas industries, refineries, ethanol distilleries, cement and fertilizer manufactures, and other heavy industries such as iron and steel.

In India, CO_2 emissions in 2004 were about 1.34 billion tonnes **(United Nations Statistics Division, 2007),** but this is set to increase by 4 – 5 times by 2030. Just over half of India's current CO_2 emissions (721 million tonnes) are from large point sources (40.1 million tonnes/year) **(Environmental Impact Assessment (EIA) 2006 and Holloway et al., 2008).**

The Indian government expects the energy sources (Coal 50%,Oil 25%, Gas 20%,Nuclear 3%,Hydro 2%) that would remain approximately stable in the near term, till 2024-2025, **(Parikh 2006).**

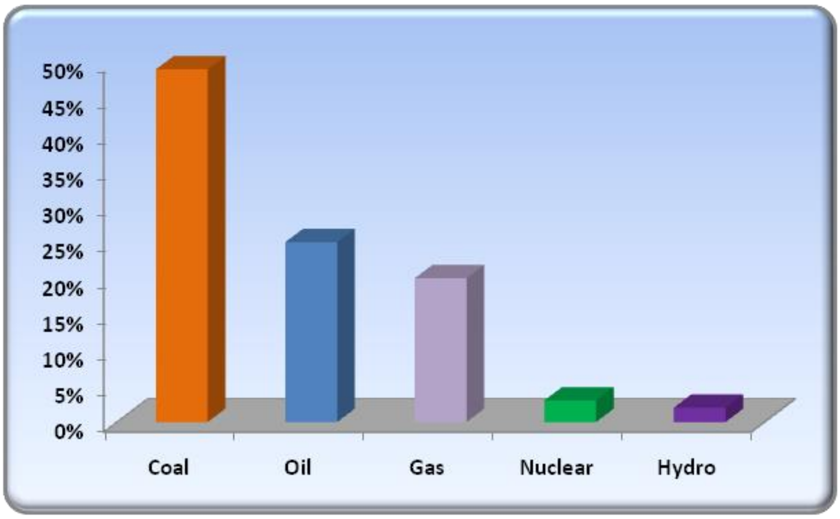


Figure 1. Projected Primary Energy mix in India 2024 - 2025

Source : Ministry of Petroleum and Gas, Hydrocarbon Vision 2025 (India Stat 2006).

1.1 Exponential growth of CO_2 concentration

CO_2 concentrations are now more than one-third higher than they were just before the industrial revolution over the past 40 years. It has been estimated that the atmospheric CO_2 content has increased by 30% from 280ppm to 380ppm during the last two centuries. This exponential growth of CO_2 concentrations are attributed mainly to burning coal, oil, and natural gas for energy production, transportation, industrial and domestic uses.

For the year 2008, coal consumption for electric power generation in the United States was found to be 1.04 billion tonnes whereas by the year 2030 US carbon dioxide emissions are estimated to reach 6.41 billion tonnes according to the EIA **(EIA, 2009)**.The total carbon dioxide emissions in the year 2007 were found to be 6.02 billion metric tonnes including 2.16 billion tonnes from coal fired electric power generation, 2.6 billion tonnes from petroleum consumption mainly for transportation, and 1.2 billion tonnes from natural gas consumption.

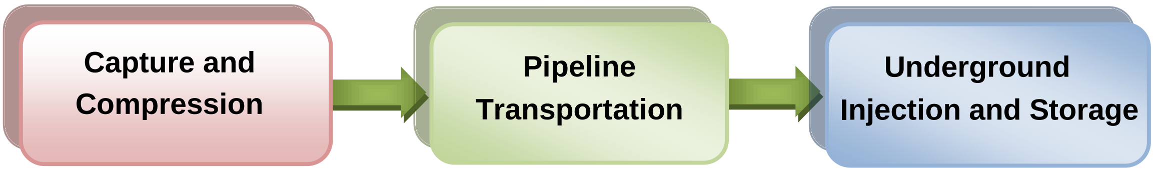
It is a well recognized fact that the concentrations of CO_2 in the atmosphere have been increasing progressively as in figure 2.

Figure 2. Amount of CO_2 in the atmosphere recorded in December 2012 at **Mauna Loa Observatory: Scripps Institution of Oceanography, Hawaii**.

Hence stringent regulations and laws are now being put in place to make sure that as we grow, the energy we use should be clean and safe and work with the environment rather than against it. This has lead to the adoption of sustainable development methods like shifting to alternative energy sources such as nuclear power and renewable energy. Renewable energy sources though are on the increasing mode, the immediate energy demand is likely to be met only by conventional fossil fuel combustion. In the light of increasing fears about climate change, **Carbon Capture and Storage** (CCS, the subject of this research work) has assumed growing importance. At present it provides a bridging technology, since it allows a balance between increasing demands for energy and the requirements to reduce emission **(Magnus Eriksson, 2009).**

1.2 Carbon Sequestration(CCS)- An Overview

The basic idea behind CCS is to capture CO_2 from large industrial sources before it is released into the atmosphere, and then carefully transporting and storing it in matured oil and gas reservoirs or in other deep geological formations like saline aquifers where it would remain for thousands of years or longer. Hence, CCS offers important potential to reconcile further utilization of fossil fuels and climate change mitigation policies, particularly in using coal for generating electricity.



Schematic showing the major steps in the Carbon Capture and Storage Process

1.3 CO_2 Capture techniques

The first step in the CCS chain is the capture of CO_2. At present, there are three main pathways for capturing CO_2 from fossil fuel energy conversion systems.

1.3.1 Pre-Combustion Capture

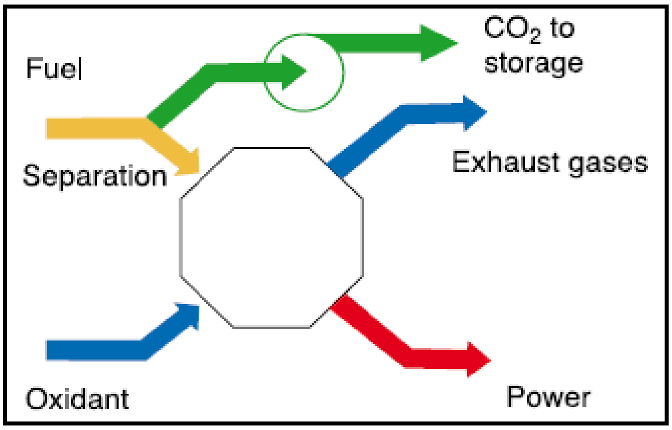


Figure 3. Schematic of pre-combustion capture (Metz *et al*., 2005)

The pre-combustion capture process includes treating the fuel either with steam and air or with oxygen (partial oxidation) to produce syngas – a mixture of carbon monoxide (CO) and hydrogen. Syngas is further oxidized to produce CO_2 and H_2O in a gas turbine during the generation of power. Also, the syngas can be sent to a shift reactor to produce more hydrogen by adding steam and removing CO_2 from the gas stream coming out of the reactor. Thus the entire process results in two pure streams of hydrogen and carbon dioxide.

1.3.2 Post-Combustion Capture

Post-combustion carbon capture process is the most commonly and widely used method, in which CO_2 is separated from the flue gas stream leaving the power plant, after cleaning the flue gas. The stream of CO_2 is then dehydrated, compressed and finally transported to its storage destination.

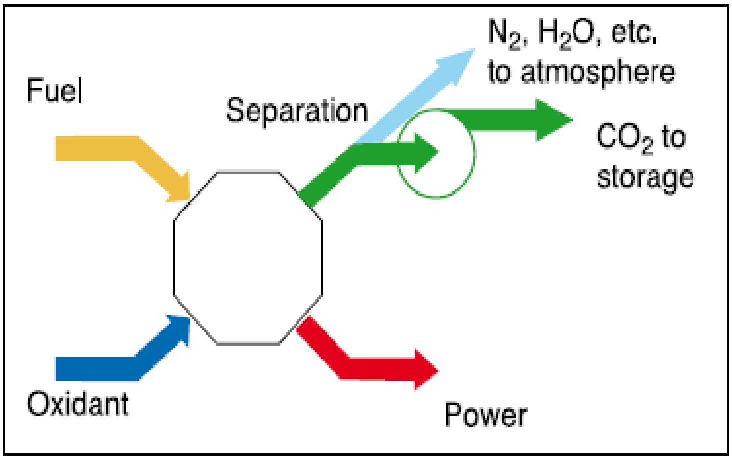


Figure 4. Schematic of post-combustion capture (Metz et al., 2005)

1.3.3 Oxy-fuel Combustion capture

Oxy-fuel combustion process involves the combustion of a fossil fuels using pure oxygen instead of air. The resulting flue gas stream comprised of mainly CO_2 and H_2O with small amounts of impurities such as Argon, Oxygen, oxides of sulphur and oxides of nitrogen. The exhaust from oxygen combustion process has a very high concentration of CO_2 which can be captured, compressed for transportation and stored

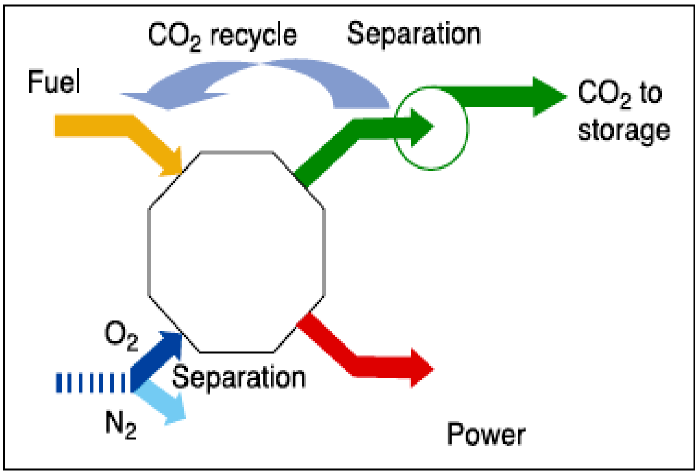


Figure 5. Schematic of Oxyfuel-combustion capture (Metz et al., 2005)

The methods for the post-combustion capture of CO_2 from flue gas include:

- Chemical absorption
- Physical absorption
- Membrane separation
- Adsorption
- Cryogenic separation

Chemical absorption -Amine scrubbing technology

The scrubbing of CO_2 by chemical absorption represents the realizable and best near-term option for CO_2 capture from power plants. CO_2 is alienated from the flue gas by passing the flue gas all the way through a scrubbing system that consists of an absorber and a desorber. Absorption process utilizes the reversible chemical reaction of CO_2 with an aqueous alkaline solvent, generally an amine. In the desorber, the absorbed CO_2 is removed from the solution and a pure stream of CO_2 is sent for compression while the regenerated solvent is sent back to the absorber.

Alkanolamines, a simple combination of alcohol and ammonia are the most commonly used chemical solvents for CO_2 capture. Monoethanolamine (MEA) is the most widely used solvent for CO_2 scrubbing units **(Anusha Kothandaraman, 2006 and Si Ali et al., 2012).**

Physical absorption- Glycol scrubbing technology

Physical solvent scrubbing of CO_2 is well established. Physical solvents are used when there is a high concentrated stream of CO_2 at high pressures. A glycol based solvent, monoethylene glycol (MEG) has been used for decades to process natural gas, both for bulk CO_2 removal and H_2S removal and effective capturing of both at higher concentration **(Davison et al., 2001).**

1.4 CO_2 Transportation

CO_2 is transported from the source of capture to the storage location using conventional pipeline technology. Normally the CO_2 is transported in the supercritical flow conditions. Depending on pressure and temperature, CO_2 can exist as solid, liquid, gas or supercritical fluid. The term dense phase is used to represent CO_2 in the supercritical or liquid state. For transporting CO_2 through pipelines the dense phase is preferred due to the fact that its density is close to that of liquid water, but its viscosity is approximately equivalent to that of gaseous CO_2.

In the majority of CO_2 pipelines, the flow is determined by the compressors at the pipeline source and with intermediate compressor stations while in progress. These make certain that the essential temperature and pressure are consistently maintained.

One which was successfully constructed was the Weyburn, CO_2 pipeline from Beulah, North Dakota, USA, to the Weyburn Oil Field in Saskatchewan, Canada **(Wilson et al., 2004).** Over 5000km of CO_2 transport pipelines have been built, and are operational mainly in the USA and also in Turkey. These pipelines have been used primarily to deliver CO_2 for Enhanced Oil Recovery (EOR).

The primary material choice to construct CO_2 transportation pipeline is carbon steel. In spite of the development of corrosion resistant alloys over the past few decades, carbon steel still constitutes an estimated 99% of the materials used in the oil industry. It is usually the cost effective option, being a factor of 3 to 5 times less costly than stainless steel.

1.5 Underground CO_2 Injection and Storage

CO_2 storage encompasses storage in terrestrial ecosystem and/or geological formations. Geosphere sinks are naturally occurring reservoirs that historically, on a geologic time basis, have been sinks for carbon. We are extracting carbon from these sinks to use for energy, thus producing the carbon energy-based economy. These same reservoirs, including deep aquifers, can be used to store carbon dioxide thereby removing the CO_2 from active participation in the global carbon balance.

The CO_2 should be injected into the underground storage facilities using downhole tubular. In general, the downhole tubular consists of casing pipe to secure the hole, which is secured by cementing to avoid contamination from other underground fluids. A smaller pipe (known as downhole tubing) is inserted into the casing through which CO_2 is injected from the surface into the well. The whole downhole system's pressure is controlled using wellhead to prevent blowout. The downhole tubular operates at higher pressure injecting the CO_2 into the storage facility overcoming the underground pressure as well as keeping the CO_2 under dense phase conditions during injection. Once injected, the CO_2 dissolves in the saline water.

1.6 CO_2 Corrosion

Corrosion is one of the main concerns in the capture, transport, and storage of carbon dioxide from flue gas. CO_2 must be dried to get rid of the corrosion risk while transporting CO_2 at high pressures using low alloy carbon steel pipelines. **(Seiersten and Kongshaug, 2005).**

Dry CO_2 is inert to commonly used industrial materials. But CO_2 which is an acid gas will react with water to form carbonic acid which is corrosive. The corrosion rate will be significant for carbon steel when carbonic acid is formed. In addition water gets saturated with CO_2 forming a solid hydrate which in turn reduces the flow and increases pressure drop, or may even stop the flow. For this reason the water content is kept low and is continuously monitored **(Papavinasam et al., 2012).**

To increase the density of the CO_2, the captured CO_2 gas is normally compressed to the supercritical state to a temperature of 31.1 °C and at the pressure of 73.8 bar thereby making it easier and less costly to transport **(Kruse and Tekiela, 1996 and Gale and Davison, 2004).**In literature, there are several studies which provide qualitative support for corrosion on carbon steel in water-saturated supercritical CO_2 phase **(Russick et al., 1996, Propp et al., 1996, and McGrail et al., 2009).**

1.7 Effect of impurity

Once injection has started, supercritical CO_2 and any other potential impurities dissolves and interactions occur between the injected stream and the well materials. Although CO_2 alone is not reactive, once in contact with brine, carbonic acid (H_2CO_3) is formed, which dissociates in the brine. The formation of this acid reduces the pH of the brine, indicating that the brine becomes corrosive to well materials, rocks and pipelines **(Gaus, 2010)**. Contamination of CO_2 can have potentially terrible consequences as it can cause major changes in the property behaviour of the gas in the pipeline. The CO_2 captured from various sources may contain many impurities depending on the process and capture technology.

The 'other components' or 'impurities' present in CO_2 streams include nitrogen (N_2), oxygen (O_2) and water (H_2O), and also air pollutants such as sulphur and nitrogen oxides (SO_x and NO_x), particulates, hydrochloric acid (HCl), hydrogen fluoride (HF), mercury, other metals and trace organic and inorganic contaminants **(IPCC, 2005).** In addition to these impurities CO_2 stream may also contain small amounts of chemical solvents (amine based solvents) used in the post-combustion capture process **(DeVisser et al., 2008).** During the scrubbing processes there is a possibility for MEA and MEG (solvent) to get into the CO_2 transportation pipeline along with CO_2 as an impurity.

Currently there is little knowledge on the effect of impurities on material properties under CCS operating conditions. Though the CO_2 is transported in supercritical conditions, aqueous water phase occurs during the shutdown period which may either accidently or due to operational requirements. In addition during the injection of CO_2 into saline underground water turbulent flow conditions are formed creating conditions for **flow-induced localized corrosion (FILC).**

Therefore, to select appropriate materials for CO_2 sequestration network, the corrosion behaviour of materials in both super critical conditions as well as at atmospheric pressure flow conditions should be understood. In addition, the influence of various impurities including O_2, N_2, SO_2, NO_x, H_2S, ethylene glycol, amines, and ammonia should also be investigated **(Papavinasam et al., 2012).**

Carbon steel and stainless steel are the candidate materials of construction of CCS network. Therefore their corrosion behaviour in the CO_2 environment under simulated flow conditions in the presence of impurities need to be investigated.

The present investigation has henceforth been taken up with an idea of understanding the corrosion behaviour of carbon steel and stainless steel in CO_2 environment under simulated flow condition and at atmospheric pressure by measuring mass loss using Rotating Cage (RC).

To understand the behaviour of pipeline materials in CO_2 environment containing solvent impurities like MEA and MEG, carbon steel of three different compositions (Carbon steel - I, 5LX 42 and 5LX 60) and two different types of stainless steel (304 SS and 316L SS) were used in the present work.

Following studies were undertaken to fulfill the objective of this research investigation,

- Compilation of literature on composition of materials used in oil and gas pipelines.
- Establishing laboratory procedure for Rotating Cage.
- Evaluating the corrosion behavior of carbon steel and stainless steel by mass loss measurements using RC in CO_2 environment under
    a) Different NaCl concentrations
    b) Different of periods of rotation.
- Impact of 4M MEA as impurity on the corrosion rates of pipe line steel in CO_2 environment with the parameters:
    a) Effect of Nacl concentration
    b) Effect of period of rotation.

- Impact of 4M MEG as impurity on the corrosion properties of pipe line steel in CO_2 environment with the parameters:

    a) Effect of Nacl concentration

    b) Effect of period of rotation.

    c) Effect of oxygen as impurity in MEG

- Comparison of the corrosion rate of carbon steel and stainless steel in the CO_2 environment.

- Surface morphology of steels in CO_2 environment through Inverted Metallurgical Microscopy, Scanning Electron Microscopy, and Energy Dispersive Spectroscopy.

- Significance of experimental data through ANOVA.

- Developing a corrosion database for material selection of pipelines under service conditions of CO_2 capture process.