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Carbon Capture and Storage Technology for Sustainable Energy

Dr (Mrs.) Malti Goel
Jawaharlal Nehru University, Centre for Studies in Science Policy, New Delhi, India

1. Introduction

Carbon capture and storage (CCS) is amongst the range of energy technology strategies for addressing concerns of increasing greenhouse gas emissions in the atmosphere and achieving sustainable energy from fossil fuel use. In the long run its potential to reduce CO_2 concentrations is second to the contribution expected from energy efficiency improvement (ETA, 2008). The main focus of this chapter is to describe the processes and techniques of CCS technology as well as challenges and policy concerns. Large-scale deployment of CCS however, raises issues of permanency and safety of storage. Consequently, enormous research efforts are directed worldwide in testing its efficacy. Results are summarized in the Indian context from the International Workshop on R&D Challenges in Carbon Capture and Storage Technology.

2. The CCS technology

Carbon dioxide is most prominent natural and biogenic greenhouse gas that trap heat in the atmosphere. Its presence at a concentration of 0.03 per cent by volume in the atmosphere is critical in maintaining the planet earth at a temperature suitable for human beings. A natural carbon balance is maintained through 'carbon cycle' in the earth system. It involves exchanges of carbon dioxide in the Atmosphere with the Hydrosphere, Biosphere and Lithosphere.

Post industrialization long-term increase in carbon dioxide content in the air is seen to be of the order of 30% since 1850, increasing from 280 ppm to 374 ppm in 2005. As the concentration of CO_2 in the atmosphere is building-up, natural carbon cycle is getting disturbed and global warming is being caused. Intergovernmental Panel for Climate Change (IPCC) provides evidence that the average earth's temperature has risen by 0.74°C, in 2005 from what it was in 1906. The rising concentrations of CO_2 are mainly ascribed to the use of fossil fuels - coal, oil and gas for energy production and consumption.

Carbon capture and storage (CCS) is amongst the range of energy technology strategies for addressing concerns of increasing greenhouse gas emissions in the atmosphere and achieving sustainable energy from fossil fuel use. The CO_2 sequestration – Carbon Capture and Storage (CCS), may be subdivided into three systems.

- CO_2 capture and compression system. This system may also comprise conditioning units for transport

- Transport system for taking the captured CO_2 to appropriate locations.
- Injection and storage system for its permanent storage away from the atmosphere. The injection system comprises wellhead(s) and the injection wells. The storage system comprises the geological formation (reservoir) in which CO_2 is injected as well as its surrounding medium (cap-rock, overburden, etc).

The various components of CCS are depicted in Fig. 1.

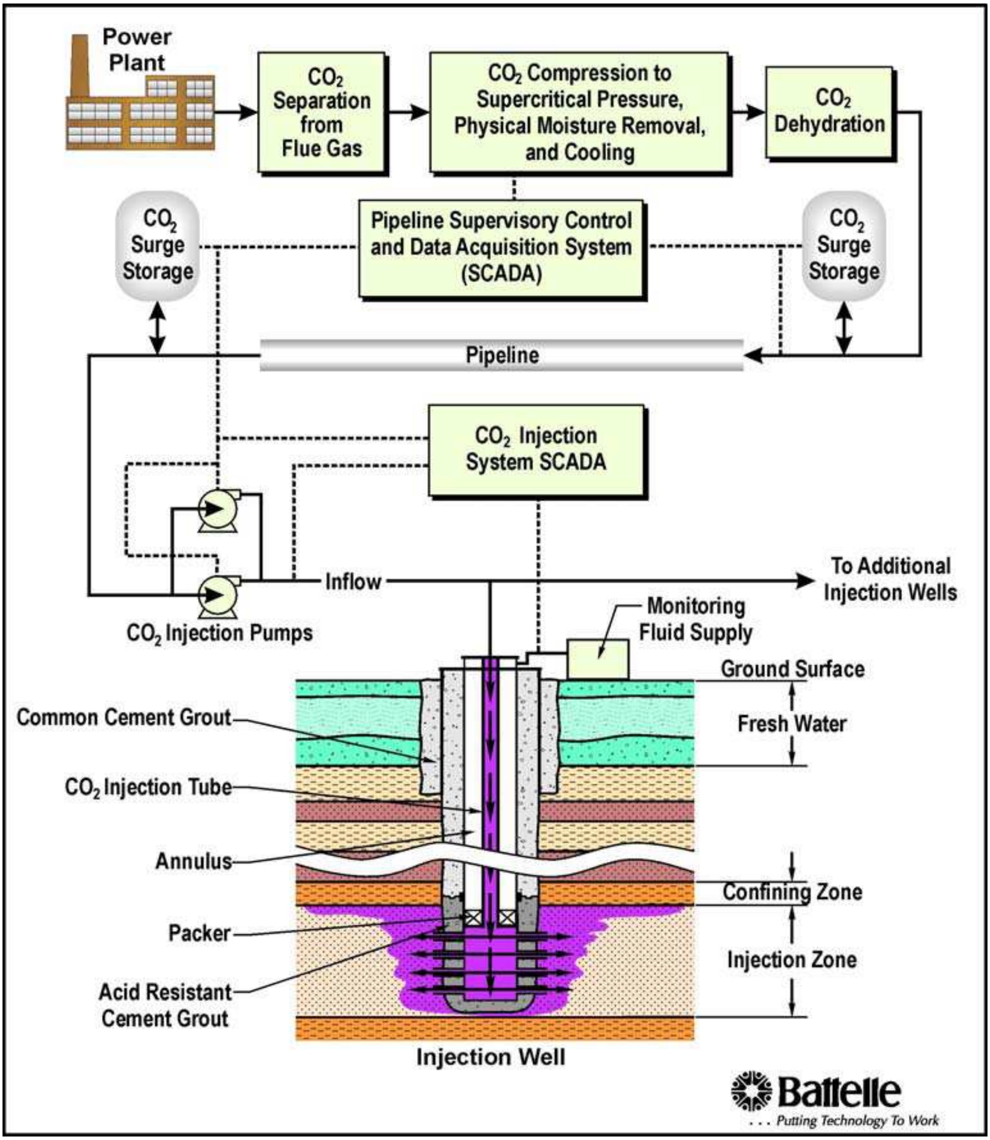

Fig. 1. Carbon Capture and Storage Technology Systems (Dooley, et al, 2006)

2.1 CO_2 capture technology

The carbon dioxide in the atmosphere can most appropriately be captured at locations where it is produced, such as thermal power plants or industrial units (Herzog and Drake, 1996). Global point sources emitting more than 0.1 Mt of CO_2 from 4492 power sources added to 10.5 Bt of CO_2 per year and 2953 energy consuming outfits added to 3.5 Bt of CO_2 in 2005 (Metz et al 2005). The CO_2 capture using chemical, physical and biological techniques can be adapted to power plant flue gas as well as to steel plants, cement works, ammonia, gas processing industries, and refineries as its other point sources. The main considerations in CO_2 capture application to a point source, besides technology are; cost and efficiency penalty. The captured CO_2 is compressed to liquid form.

2.1.1 CO_2 capture from the flue gas of a coal power plant

Coal is having relatively highest carbon-to-hydrogen ratio among other fossil fuels and therefore its use results in higher CO_2 emissions per unit heat output than oil or natural gas. Three basic options for CO_2 capture are distinguished as post-combustion capture, pre-combustion capture, and modified combustion (oxy fuel and chemical looping) processes. A schematic of CO_2 capture process is presented in the Fig. 2. Chemical and physical separation using: absorption in solvents, adsorption on solid sorbents, membrane separation and cryogenic processes, are developed or developing.

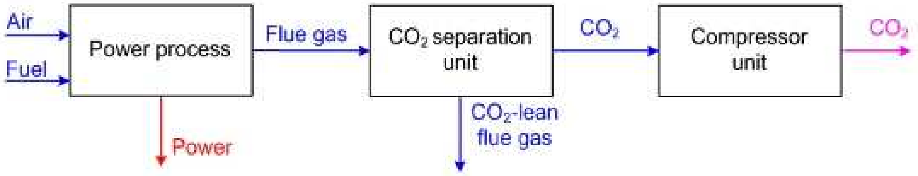

Fig. 2. Schematic of CO_2 capture process.

Post-combustion flue gas from a coal based thermal power plant comprises of 8-14% CO_2. At such low concentrations of CO_2, chemical absorption processes are more reasonable. Amine based CO_2 separation technologies are commercially proven and are industrial bench mark. The power plant flue gas reacts with amines at 40 to 60°C, but the process of CO_2 separation from the CO_2 rich solvent needs higher temperature. The solvent can be recycled after use. The advantage is that CO_2 is recovered up to 90% purity and recovery rates are 98% (Yamasaki, 2003). This process is also known as scrubbing or absorption-stripping of flue gas stacks.

Monoethanol amine (MEA) and diethanol amine (DEA) impregnated activated carbon, zeolites and alumina have been studied for adsorption, desorption and thermo-gravimetric evolved gas analysis of CO_2 saturated samples with further optimization in progress (Jadhav, et al, 2008). Amine processes have high energy penalty and the cost of electricity increases by as much as 70%. Low partial pressure, high temperature of flue gas and presence of other gases are some of the other key problems encountered in their use. Polymer system amines like amine functional polystyrene perform better and can be regenerated at a lower temperature of the order of 60°C temperature (Chakma, 1997). Amine functionalized materials including natural biopolymers and synthesized nitrogenous activated carbon offer vast scope in reducing energy penalty for CO_2 capture (Gattuso, 2007). Activated carbon offers useful sites for CO_2 absorption at atmospheric temperature as well as at high temperatures (temperature of the flue gas).

To offset some of other limitations of solvent based separation i.e. high solvent losses by evaporation and high rate of corrosion of the equipment, search for novel solvents is on. The approach to develop immobilizing liquids disposed upon different solids has been studied (Mahosan, et al, 2008). Enhanced absorption studies carried out for gas separation using multi-phased absorbents that are composed of porous solid support having a liquid phase in CO_2 capture are reported.

Commercially proven as gas purification technology, membrane technology for CO_2 separation is under development. Membrane separation process can perform in two ways; either a membrane filters CO_2 or it filters gases other than CO_2 by a solution-diffusion mechanism. Materials for membranes with preferential CO_2 transport include functionalized polymers, metal organic framework and polymer composites. These operate close to ambient temperatures. Powell and Qiao, 2006 presented a review on performance of CO_2/N_2 gas separation polymeric membranes, their permeability and selectivity properties.

Porous and non-porous inorganic nano-membranes offer new possibility of integration with power plants to provide cost-effective CO_2 capture solutions. Recent developments include polymer-inorganic hybrid membranes and nanostructures for higher efficiency and reduction of total cost for CO_2 capture. Pyrolysis of thermosetting polymers can lead to carbon molecular sieve membranes with pore size distribution below the molecular dimensions. These materials can be supported on alumina to improve their mechanical stability. Ionic transport membranes are also under development.

Application of Pressure Swing Adsorption (PSA) to separate CO_2 from other impurities would reduce the energy consumption of CO_2 separation by 25-30%. Moreover, Pressure Swing Cycle can be applied for both post-combustion and pre-combustion capture, if CO_2 concentration is high. The adsorbent gets saturated with CO_2 and subsequently regenerated yields very high purity CO_2 (90%). A recovery up to 78% is expected. Simulation of this cycle with a hydrotalcite adsorbents of 0.85mol/kg CO_2 capacity at 575 K, shows promising results and potential of PSA processes for still higher CO_2 recovery (Goswami, et al, 2008). Recent studies on carbon dioxide adsorption over Ca/Al hydrotalcite and Mg/Al hydrotalcite have been reported in the temperature range 40 to 800°C, at different pressures and mol ratio (Gaikwad, 2010). Further work is required in development of non-conventional PSA cycles for CO_2 separation and study of behavior of Hydrotalcite materials.

2.1.2 Advanced CO_2 capture options

New Class of nano-materials, which selectively attract CO_2 molecules at 220^0C, i.e. nearer the temperature at which water gas shift reaction occurs in IGCC are being developed. Zeolites as crystalline luminium silicates are effective membranes for a wide range of CO_2 separation applications. In the advanced Integrated Gasification Combined Cycle (IGCC) "synthesis gas" (mainly $CO + H_2$, plus some CO_2) produced from coal gasification process undergoes a further catalytic "gas-shift" process with water vapour transforming most of the CO into additional CO_2 and H_2. The capture of CO_2 is then combined with the necessary purification of hydrogen. Hydrogen, together with the non-shifted CO acts as the feed for a combustion gas turbine for producing electricity. The cost analysis of adding CO_2 capture to various options viz., a IGCC plant, pulverized coal fired plant and supercritical coal combustion has been studied (Narain, 2008).

Zeolites are crystalline aluminum silicates as effective membranes for a wide range of CO_2 separation applications. New class of nano-materials, which selectively attract CO_2 molecules at 220°C, i.e. nearer the temperature at which water gas shift reaction occurs in IGCC are being developed. In order to identify possible options, binding energy estimates and thermo gravimetric analysis are used as screening tools. Nanostructures for the abatement of carbon dioxide (CO_2) at the pre-combustion stage of gasification-based power generation include lithium silicate nanoparticles and membranes that consist of CO_2-philic ionic liquids encapsulated into a polymeric substrate (Pennline, et al, 2008).

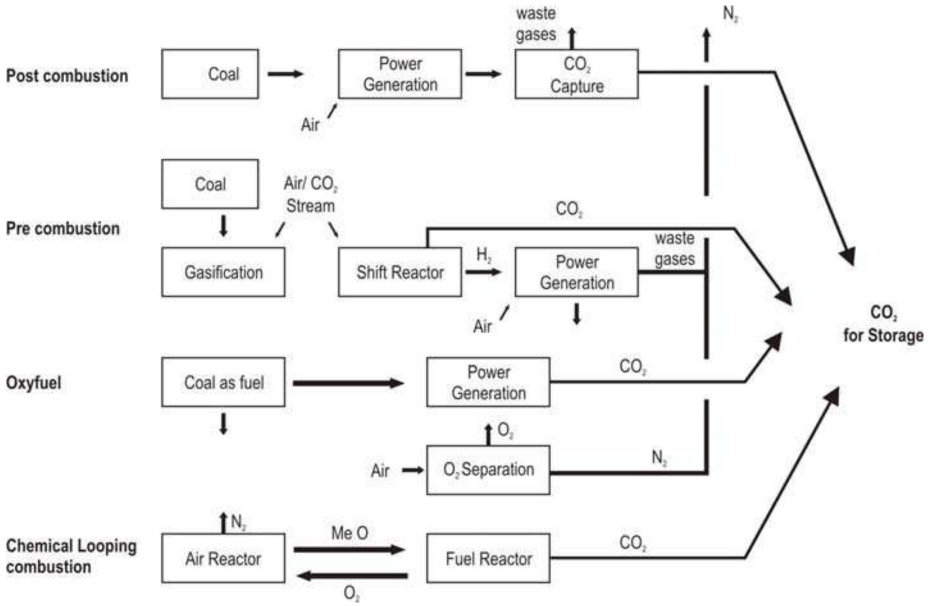

Fig. 3. CO_2 capture; pre combustion, post combustion, oxy-fuel combustion and chemical looping combustion (Goel, 2008)

Modified combustion processes are the other options being developed to increase the efficiency of coal based generation and concentration of CO_2 in the flue gas. In a highly oxygen enriched atmosphere used in oxy fuel combustion, the thermal ballast is recycled CO_2. The other advantage is that the flue gas in this case is essentially composed of CO_2 and water instead of nitrogen from air. It does not require separation of inert gases normally present. The energy penalty in this case comes from the additional cost of the air separation process, which is necessary to produce oxygen for combustion.

First CCS power plant based on oxy fuel combustion is Sask Power project, using Saskatchewan lignite. Low sulphur content in coal/ lignite does not required internal desulphurization in the fuel gas recycle loop of an oxy fuel plant. A 0.3MW pilot scale project capture ready power plant planned near Ottawa has been started to demonstrate oxy fuel combustion with CO_2 capture. Another oxy coal combustion pilot plant facility of 30MW has been demonstrated in Germany (Vattenfall and Alstom) in 2008. Oxy-fuel Firing is expected to develop for high ash coals as one of the best solution for carbon capture among other options (Timms, 2007).

Research is also being conducted in advanced coal based technologies like molten carbonate fuel cell, chemical looping combustion etc. for mitigating CO_2 emissions. The chemical looping combustion (CLC) has advantage of inherent CO_2 capture. The CLC has two reactors, one for air and one for fuel as depicted in Fig. 3. In the air reactor carrier is oxidized by oxygen and in the fuel reactor metal oxide is reduced by the fuel. Flue gas from air reactor contains N_2 and unreacted O_2. Exit gases from fuel reactor contain CO_2 and H_2O, pure CO_2 can be separated, whereas H_2 is combusted (Mattison and Lyngfelt, 2001).

2.2 CO_2 transport

Once the CO_2 is captured and compressed, it can be transported to storage sites. The transport of CO_2 is not a scientific problem. Pipelines and ships are considered the most likely means of long distance CO_2 transport. Using existing oil pipelines facilities is the most feasible transportation option for distances up to 1000 km. Shipping of CO_2 for longer distances or overseas would be similar to shipping liquefied natural gas. In the absence of oil pipeline networks, new high pressure pipelines are major infrastructure costs. The pressurization energy requirement and recycling of CO_2 at the receiving end also add to the cost.

2.3 CO_2 storage

For geological storage CO_2 is injected underground in a variety of geological environment in sedimentary basins. Within these basins oil & gas reservoirs and empty fields; unmineable coal seams; and saline formations are possible sites. Other potential storage sites for sequestration of carbon dioxide include caverns, basalt rocks and organic shales. These kind of geological formations are found both on and offshore in various locations around the world. To achieve successful storage in terms of mitigating the damaging environmental effects of CO_2 accumulations in the atmosphere, such storage must be relatively permanent. Permanence would means that the CO_2 does not leak back into the atmosphere at any significant rate for hundreds to thousands of years. To achieve this injection of CO_2 must take place at depths in excess of 800 metres so that geological cap rock can prevent the gas from migrating back to the surface.

Injection of CO_2 is done using infrastructure and experience of oil industry. Innovation is also taking place. Carbon micro-bubbles can be injected as atomized foam and this allows dispersal deep into tiny pores of different underground structures and makes it a stable and leak proof process (Koide and Xiu, 2009). The R&D needs with respect to injectivity, reactive fluid, transport reservoir monitoring etc. for CO_2 sequestration, (which are likely to become an important part of exploration & production operation in oil fields) have been identified based on results obtained from the FRIO project (Hovorka et al, 2005). where in 600 tonnes CO_2 was injected in geological formations and has been monitored.

The carbon dioxide exists in gas, liquid, solid and supercritical phase. The pressure-temeperature phase diagram is depicted in Fig. 4. The CO_2 is normally stored underground in super-critical phase, which is attained at 31.1^{0}C temperature and at pressure greater than 73.9 bars. It has properties in between gas and solid with following characteristics.

- Dense gas
- Physico – chemical properties between those of liquid and gas.
- Solubility approaching liquid phase
- Diffusivity approaching gas phase

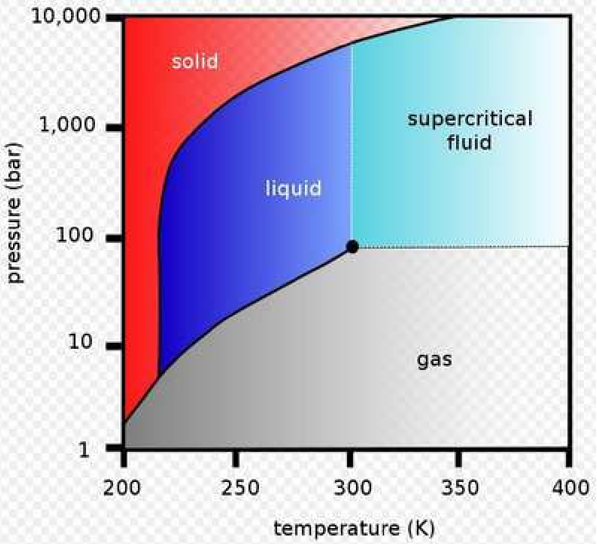

Fig. 4. Pressure-temperature phase diagram of CO_2

2.3.1 Trapping mechanisms

Inside the earth, pore space between the rock grains or minerals is occupied by fluids. Open fracture and cavities are also filled with fluid. These act as trapping sites. Depending on the permeability and thickness of the formation, CO_2 injection raises the pressure near an empty reservoir the well, allows the liquid gas to enter pore spaces. The CO_2 may either dissolve in or mix with the fluid, displace the in-situ fluid or react with mineral grains or combination of the processes may occur. In case of saline aquifers, CO_2 solubility in formation water decreases as temperature and salinity increases. The CO_2 dissolved in water can form $CaCO_3$ and it also reacts with sodium, potassium, silicates, magnesium etc. Reaction can be rapid in case of carbonate materials, but slow in case of silicate materials. Once formation fluid is saturated with CO_2, its absorption slows down and is controlled by diffusion and convection. The CO_2 storage process changes the reservoir properties. Thus different trapping mechanisms for injected CO_2 are expected to occur.

Structural / Stratigraphic trapping – When CO_2 is pumped under low permeable rock conditions it rises up until it reaches top of the formation. Below the impermeable cap rock trapping occurs in the structural faults and in between two stratified layers. The drilling wells are resealed with steel and cement caps.

Hydrodynamic / Residual trapping – Residual trapping occurs when liquid CO_2 becomes stuck within the pore spaces of the rock, which has sponge like structure. It remains confined to an immobile phase.

Geochemical / Solubility Trapping – Injected CO_2 forms a bubble around the injection well, displacing mobile water laterally and vertically. The interaction between fluids or salty water contained in the pore spaces of the formations allows geochemical trapping mechanism to take effect. Geochemical trapping is relatively permanent but slow process. CO_2 undergoes sequence of geo-chemical reactions, first reacts with water and then residual CO_2 trapping may occur with in-situ fluid.

Mineral Trapping – Over time CO_2 that is not immobilized by residual trapping, can react with in-situ fluid to form carbonic acid (H_2CO_3) that dominates for tens to hundred years. Dissolved CO_2 can eventually react with surrounding minerals, if the appropriate mineralogy is encountered. It forms carbon bearing ionic species HCO_3^{-1} and CO_3^{-2} also known as ionic trapping. It dominates for hundred to thousand years (Fig. 5).

Further breakdown of the ionic minerals could precipitate in carbonates ($CaCO_3$) that could fix injected CO_2 over thousand to million years. Multiple trappings can lead to rock formation through conversion into carbonates, magnesite and Kaolins etc, which are the main components of natural rocks. This being most permanent fixation of CO_2, the reaction rate can be enhanced and the kinetics of reaction mechanism can be understood. Preferred storage mechanisms for different geo-environments are depicted in Table 1.

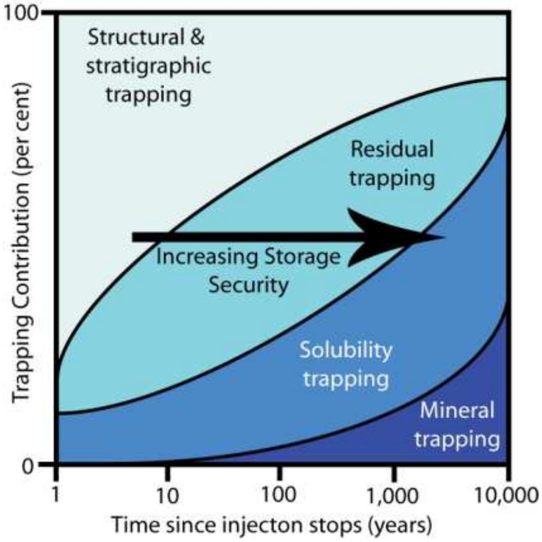

Fig. 5. CO_2 underground trapping as a function of time (source – IPCC 2005)

S. No.	CO_2 Subsurface reactions	Preferred Geo-environment
1.	Structural & Stratigraphic	In Natural gas reservoirs
2.	Hydro dynamic trapping	In saline aquifers, gas reservoirs
3.	Solvability trapping	In oil reservoirs
4.	Mineral trapping	In brines, Basalt rocks

Table 1. CO_2 underground trapping mechanisms and preferred environment

Technologies such as Geographical Information System (GIS) are useful tool for mapping of CO_2 sources and analyzing potential for its storage sites (Holloway et al, 2008). Storage capacity in possible underground locations has been assessed. The process of Enhanced Oil Recovery (EOR) using CO_2 is an active process and how it can help sequester the carbon dioxide at a low net cost is being tested in Canada's Weyburn Oil Fields. In the coal beds, enhanced coal bed methane (ECBM) process can increase the recovery from CO_2 injection up to 90%.

2.3.2 CO_2 storage possible sites – basalts, saline, empty gas fields, empty oil fields

Basalt formations are solidified lava and have unique chemical properties. In Basalts, carbonation rate at equilibrium with supercritical CO_2 in pore water is higher as compared to other sedimentary rocks such as day feldspar (McGrail el.al. 2006). Subsurface reactions with minerals to from carbonate precipitations are being looked as possible long-term fixation. Research carried out in Columbia River Basalts suggests that lateral dispersions and vertical transport of CO_2 to overlaying basalt flows are expected to be important limiting factor controlling in-situ process. Pacific Northwest National Laboratory, USA has identified carbon dioxide sequestration research priorities in flood basalts in Columbia river region. Simulation of gas phase saturation is depicted in Fig. 6. Considerable further research is needed to understand the kinetics of rapid mineralization reaction rates that may occur in different basalts across the world.

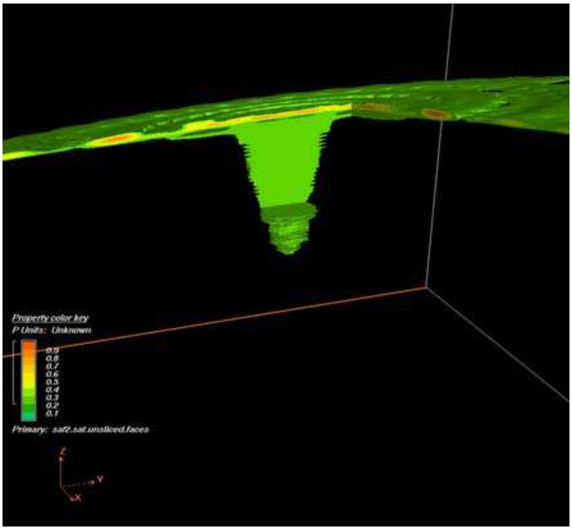

Fig. 6. Simulation of gas phase saturation in Basalts (source - Pacific Northwest National Laboratory, McGrail, et al, 2008)

Deccan Province in West India is one of the continental flood basalts covering an area of 500x10^3 sq.km and one amongst the largest flood eruption in the world. Thickness varies from a few hundred m to 1.5km consisting of the thick Mesozoic sediments, below which could show accelerated reaction with CO_2 and its conversion into mineral carbonates (Kumar, et al, 2008; Prasad et al, 2009). Similar to Columbia river basalts in composition, the basalts are expected to form a good cap rock to the reservoir. However, this region is seismically opaque and therefore difficult to monitor. One of the research areas is identified as role of vesicles in vertical carbon flows and enhanced reactivity.

Saline aquifers provide large CO_2 storage capacity. Major bottlenecks are; lack of knowledge about their structure and physical properties as well as the behavior of CO_2 in the subsurface saline reservoirs aquifers. The studies so far are site specific and need to be evaluated on case to case basis. Considerable additional geological investigation would be needed to create data base for effective mapping of such reservoirs. One of the first saline aquifer storage projects is in Norway. CO_2 from Sleipner Vest field is being sequestered in the North Sea into a shallow subsurface aquifer below seabed in Utsia. About 3000t CO_2 per day (1Mt/year) has been injected into an aquifer at a depth of 1000m just above the production reservoir since 1996. Total 20Mt of CO_2 is expected to be sequestered at this site. The CO_2 flow is constantly monitored to see its impact.

New experiments are under planning. A large commercial sequestration project is under planning stages at Gorges fields of NW of Australia. It is proposed that 10,000 tons of CO_2 per day could be injected into the deep saline aquifer. Empty gas fields and empty oil fields are other underground storage options.

2.3.3 CO_2 utilization in recovery of energy fuels

An important aspect of carbon sequestration is recovery of value added products while CO_2 is injected in oil or coal fields.

2.3.3.1 Oil reservoirs

In geological storage of CO_2 in Enhanced Oil Recovery (EOR) project, injection wells are most critical areas requiring study of mechanisms to determine the potential of oil recovery. To assess oil displacement various mechanisms are involved; oil swelling, viscosity reduction, miscibility generation and reduction in residual oil saturation. Relative contribution of various parameters depends on the reservoir conditions and crude oil quality. The CO_2 in oil well can be either miscible or immiscible phase depending primarily on the pressure of injection gas into the reservoir. In miscible phase injected CO_2 can mix with the viscous crude causing it to swell. It reduces viscosity while increasing reservoir pressure thus helping to produce more oil. In immiscible phase CO_2 does not dissolve in crude, the pressure is raised and helps to sweep the oil towards production well. A combination of both miscible and immiscible phases can occur for CO_2 sequestration.

First CO_2 – EOR scientific research project was started way back in 1972 in USA with the objective to recover more oil using different approaches. In this CO_2 from Natural gas fields was used. In 1986, CO_2 purchased from ExxonMobil was injected in an oil field in Colorado. This experiment also provided a test for efficacy of CO_2 sequestration, as it was mentioned that Weber Sandstone reservoir has good cap rock, making this oil field a high quality long-term sequestration site, beside enhanced oil recovery. The injection of CO_2 for its sequestration from a syn-fuel power plant has been established at Weyburn oil fields in Southern Saskatehewan, Canada while obtaining enhanced oil recovery. Weyburn field projections have suggested that CO_2 flooding has proved more effective in oil recovery as compared to water flooding. In addition, injecting about 6000 tons of CO_2 per day, 20Mt of CO_2 is expected to be sequestered (Vargas, 2009).

Another international project on CO_2 sequestration for enhanced oil recovery is In Salah, Algeria. It is expected that 17Mt of CO_2 could be injected in the gas leg of the reservoir into the oil field till the project completion in 2020. Laboratory scoping studies have also been carried out in India in a mature oil field of Ankleshwar and preliminary results from application of CO_2 EOR have revealed that incremental oil recovery by CO_2 injection is possible over water-flooding under immiscible displacement conditions, which may lead to enhanced recovery of up to 4.5% over the project life span of 35 years. By one estimate 7.5 Mt of CO_2 could be sequestered over the project life. A study on thermal EOR monitoring in heavy oil fields of Oil and Natural Gas Commission (ONGC) was conducted (Dimri, et al, 2008) under NGRI-NTNU project (Indo-Norwegian collaboration). Time lapse analysis for monitoring of fluid flow dynamics may help in optimizing the production and injection strategy.

Some of the future EOR projects are; Joint projects of Monash Energy and Shell for 35,000t/day CO_2 sequestration project in Australia, and BP CO_2 sequestration project envisaging CO_2 injection form a gas based power plant into North Sea Miller Oil field for oil recovery operation. In addition to these, Shell oil and Statoil have announced two large CO_2 EOR projects and BP plans to have another project on gasification of petroleum coke, an abundant byproduct of the oil refining process. It is envisaged that 90% CO_2 emissions will be captured and injected for enhanced oil recovery. EOR operations and CO_2 injection rates need a balance for optimizing the delivery and vary from site to site.

2.3.3.2 Coal beds

Coal and lignite may act as permanent storage for CO_2 in view of its affinity to coal molecules. Research in this area is in infancy. In a recent study conducted in USA, 90t of CO_2 injected into a Burke Country coal 3m thick seam at a depth of 300m, remained contained for 3 months. Although there were no results presented in the workshop on technical feasibility of enhanced coal bed methane recovery, some of the preliminary analysis made for enhanced gas recovery from coal beds in India, suggested that deep seated unmineable coal beds could have storage capacity of up to 120 Mt (Singh, 2008). Stimulated gas production profile for gas recovery through CO_2 injection in a laboratory simulation on coal samples from Southern Part of Raniganj Coalfield has been carried out (Mendhe, et al, 2008). Stratigraphic horizon of coal deposits in India and possibility of further research on coal bed methane from CO_2 storage in coal seams need to be demonstrated. In depth studies on geological, geo-morphological and physio-chemical studies of reservoirs and cap rocks are required to address the questions like; whether carbon dioxide will remain entrapped, for how long and what coal types are suitable?

3. Future challenges

Huge amounts of natural gas are expected to be trapped in condensed form in the gas hydrates. The gas hydrates are non stiochiometric inclusion compounds in gaseous molecules, which exist as a solid phase at high gas pressures and low temperatures deep inside the oceans. The gaseous molecule can be methane or carbon dioxide or any other. Recovery of hydrocarbons from methane gas hydrates is yet a challenging task. Formation of carbon dioxide clathrates in fluid inclusions can be a mechanism of CO_2 sequestration (Prasad, 2008) while recovering methane.

Other challenges in sustainable energy lie in production of hydrogen based power with carbon dioxide capture and storage (Wright, 2008). First industrial demonstration of 475 MW capacity using hydrogen as fuel to generate low carbon power is in planning stage. Green Power generation using hydrogen from Natural gas with CO_2 capture & storage up to 1.8 Mt/ year is expected. Carson Hydrogen project is another industrial scale 500 MW project of hydrogen manufacture from Petroleum Coke with CCS facility. It is estimated that 4Mt/year of CO_2 will be injected underground, while hydrogen will be used to produce power.

A number of other breakthrough ideas and innovative concepts have been suggested for mitigating carbon dioxide in the atmosphere. A pilot integrated converter has been conceived in which magnesium can be recycled partly for energy and partly utilized for value added products. The oxygen is produced as a by-product. A magnesium carbon dioxide (Mg-CO_2) reactor could reduce 44g of CO_2 to 12g elemental carbon (Chandra, 2008). Elemental carbon has versatile applications ranging from laser research to produce exotic materials like fullerenes and carbon nanotubes (Goel, 2009).

Oil-shale is another possible option for CO_2 sequestration and is also an alternate energy source to deal with the oil crisis. In oil shale production when oil shale *kerogen* is pyrolyzed, CO_2 is co-produced. Colorado School of Mines has estimated that World oil shale resources are likely to consist 15 trillion barrels of hydrocarbon products. The Green River valley has 3,000,000 barrels resource. In an effort to control release of CO_2 from an in–situ oil shale industry, a model for CO_2 separation and sequestration has been developed (Boak, 2008). Studies have been carried out to reduce the fraction of CO_2 and develop CO_2 sequestration schemes along with production of oil shale. More work is needed not only to define its potential energy resource from underground, but also in defining the rock potential for storage. As the oil shale production grows it will be necessary to identify, secure and link large-scale target formations for these volumes of CO_2 sequestration.

4. Infrastructure issues

4.1 CO_2 capture

A thermal power plant as a point source has a long lead time of 5-6 years for putting in place the necessary infrastructure. Planning for CO_2 capture should be done in advance. This would require proper site selection and adequate space for capture components. Adequate infrastructure is required for the success of the operation. Cost-effective technologies and engineering systems are needed to capture CO_2 emissions. CO_2 Capture can become an industry standard only after technology is proven and necessary regulations are in place.

A conceptual journey on how to make a transition towards capture ready power plants has been suggested (Lucquiaud and Gibbins, 2009). Major requirements for CO_2 Capture Ready plant regardless of the CCS technology chosen for the retrofit are identified as:

i. A study of options for CO_2 capture retrofit and potential pre-investments;
ii. Sufficient space and access for the additional facilities that would be required;
iii. Identification of reasonable route(s) to storage of CO_2.

4.2 CO_2 transport

Taking part in CO_2 –EOR is considered a way forward for the future survival of fossil fuels based energy industry. Initially thought as an option to mitigate CO_2 emissions using existing infrastructure of oil & Gas industry (storage in depleted oil & gas reservoirs and transportation of CO_2 using existing pipelines) the experience suggests that new infrastructure would be required not only in power plant construction, but also in transport and at the appropriate location of storage.

4.3 CO_2 storage

4.3.1 Geo-modeling

Geo-modeling studies are carried out to model the reservoir in terms of its various parameters such as depths, size cap rock characteristics as well as CO_2 behavior in the reservoir. Although oil & gas fields offer promising energy fuel opportunities it is saline aquifers, which have highest storage capacity. Performance prediction of CO_2 behaviour in these reservoirs can be made by using theoretical models. A range of models have been developed to study CO_2 geochemistry, leakage pathways and trapping mechanisms, such as CO2PENS, STOMP, FEHM, PNLCARB, TOUGH and others, which can predict the ability of a geologic formation to sequester CO_2 as follows (Jain, 2010).

- GEO-SEQ is aimed at improved prediction of injectivity and capacity of saline formations.
- CO2PENS takes a broader view and analyzes the entire CCS operation from capture of CO_2 through transportation to injection and trapping in the reservoir.
- The STOMP-CO_2 is numerical multiphase CO_2 flow and transport simulator for modeling behavior at CO_2 of in different geo-environments. Phase behavior algorithms for physiochemical properties of CO_2 in supercritical region were added to stimulate deep well injection.
- TOUGH is a simulator development of fluid dynamics, geochemistry and geomechanics to track multiphase flows of water/ CO_2/ NaCl mixtures for application to studies of reservoir dynamics, storage capacity, CO_2 leakage, mineral trapping & cap rock integration.
- PNLCARB adopted a semi-analytical modeling framework to simulate deep-well injection of CO_2 for geological sequestration. Studies were conducted on radial injection of supercritical CO_2 in deep well formations, and tracking its multiphase flows.

4.3.2 Measurement, monitoring & verification

The CO_2 injected beneath the ground is to be carefully tracked through measurement, monitoring and verification (MMV). As many as twenty parameters have been identified for monitoring to achieve safe CO_2 storage using physical and chemical characterization techniques starting from the site selection. Site location and its characterization require scientific study in following domains.

- Sub surface domain– characterization of reservoirs and well bores to study deep migration and behavior of stored CO_2.
- Near surface domain – geological site description, seal properties, study of water quality samples to verify non seepage into shallow aquifers and soil.
- Atmospheric or surface domain –to characterize the atmospheric monitoring of gases in the area before injection and after injection.

Surface characterization is done to know about future possible leakages into atmosphere. After injection of CO_2 at a depth of 800m or so, seismic surveys by electromagnetic and gravitation sensors distributed on the surface of boreholes for storage integrity studies are carried out. The CO_2 flow and transport process in porous media, and how the cap rock seal behaves over very long time scales are the other parameters to be investigated.

Various geophysical tools such as seismic for imaging the acoustic velocity structure, gravity for imaging the density distribution, and electromagnetic (EM) methods for imaging the electrical resistivity structure are available. Electromagnetic methods are particularly useful for imaging the fluid contents of potential reservoir rocks, because electrical resistivity is largely controlled by pore fluids, porosity, pore connectivity, and, to some extent, by temperature. Different EM methods have previously been used for characterizing reservoirs. Electrical resistivity tomography (ERT) is widely used for shallow investigations. Passive magnetotelluric (MT) methods utilize natural electromagnetic fields, are typically applied for deep crustal-scale investigations. However, because of their sensitivity to electrical conductivity, noise levels are very high. Controlled-source electromagnetic (CSEM) prospecting techniques have received considerable attention for land-based imaging of different exploration targets (Sreitch, Becken and Ritter, 2010)

Well completion integrity such as cementing, injection equipment completion, are important parameters for safety of storage. At present no wells are proved to be leak tight, when exposed to supercritical CO_2 over a period of 1,000 years. Seal Integrity of cap rock is most important issue in CO_2 storage (Sengul, 2008). Well completion integrity such as cementing, injection equipment completion, and accessories are important parameters for characterization. All cement based materials are vulnerable to the attack of atmospheric or subsurface CO_2. Proper completion of an injection well should be planned initially as long-term storage requires well completion design to be safe and strong.

Otway Basin Pilot Project has been the first structured monitoring and verification project launched as geo sequestration project in Australia. Up to 100,000 tonnes of CO_2 is expected to be injected into a depleted gas fields (Sharma and Rodds, 2008). Predictive modeling studies have been developed for the sub-surface movement of stored CO_2 for many years into the future. Injection of CO_2 began in OTWAY basin of Australia in April 2008 and in the first year 4000 mt of CO_2 was injected.

Geophysical, geochemical and geo-mechanical characterization and modeling studies of heterogeneities in different types of geological formations ranging from deep saline aquifers, unmineable coal beds and mature gas and oil fields are necessary for identification of suitable storage sites. Geo-statistical behavior of reservoir and fluid flow simulations are made to test efficiency of possible storage in deep aquifers. The mineralization rate and the process in the cap rock as well as in underlying rock formation have greater capacity for mineralization and can sometime breakdown cap rock integrity. Multistage monitoring data integration would form the basis of successful CO_2 project site selection and safe storage. New tools for monitoring enhanced oil recovery using time lapsed 4D seismography are developing.

5. Geo-engineering approaches

In addition to underground CO_2 storage, geo-engineering approaches have been suggested for finding low cost solutions for CO_2 sequestration. Three ways to accelerate the natural process of CO_2 absorption are; (i) enhanced mineralization of olivine / silicate rocks (Schulings and Krijgsman, 2006). (ii) in the biosphere through enhanced genetically modified bio-sequestration, and (iii) in the oceans as artificial iron fertilization. Biochar strategy for bioenergy production with CO_2 sequestration is also proposed.

5.1 Stimulated weathering of mineral rocks

The CO_2 fixation by mineral carbonation is a process of chemical weathering in the silicates rocks of magnesium and calcium. These metal oxides and silicates are present in the earth's crust as serpentine [$Mg_3Si_2Os(OH)$] and olivine [Mg, $FeSio_4$)]. They are also present in small quantity in some industrial wastes. CO_2 reaction with such calcium, magnesium or iron bearing alkaline silicate rich rocks in a two step process to produce carbonates, is as follows:

$$(Mg.Ca)_xSi_yO_{x+2y} + H_2O + CO_2 \text{-----} (Mg,Ca)CO_3 + yCO_2$$

The cations (CO^{-2}) react with HCO_2 to form carbonates. Mafic and Ultramafic rock minerals, olivine, pyroxene and anorthile are present in large quantity in the subsurface environment. These minerals play an important role in the natural *carbon cycle* and natural weathering occurs over geological time scales. To test efficacy of artificial weathering, pilot experiments are being carried out to study mineral reactivity, energy balance, type of CO_2 injection and dynamics of CO_2 in pores.

Naturally occurring silicate materials like forsterite, wollastonite and synthetic magnesium silicates have been studied by intense grinding in presence of gaseous CO_2 (Zhana et al, 2010). In a biomimetic process (Liu et al, 2005) enzyme carbonic anhydrase as catalyst was used to accelerate the rate of precipitation of mineral carbonate with industrial wastewater as cation source. Biomimetic approach helps to develop on-site scrubber that could provide a plant-by-plant solution to CO_2 sequestration and would eliminate transportation cost. Rock-Eval analysis (Garcial et al, 2010) to quantify carbonation yields has revealed that high reactivity of system will rapidly obstruct pore space volume in an ultramafic formation with important consequences in terms of reactivity and injectivity. Effects of CO_2 fugacity and salinity impact on the kinetics of olivine diffusion have been investigated. Results suggested no inhibition effect of these parameters. Dissolution kinetics depends on pH at any temperature and would control effective mineralization process.

Mineral carbonation process is an interesting concept which involves storage of CO_2 as stable environmentally safe material. Chemical reactions produce carbonate minerals, which are stable and can be deposited on earth. The advantages are that fixation is permanent and the potential is large as the material, either manmade or natural, is freely available. The carbonation process is however energy intensive and need more field studies on the ways to assess its technical feasibility.

5.2 Enhanced bio-sequestration

Biological routes of CO_2 fixation offer new breakthrough concepts as cost-effective options. It provides an opportunity for both active and passive storage. Enhanced CO_2 absorption rate in vegetation and cropland can lead to active storage. It can be a passive storage in wetlands, mined or un-mined forest sites and high way construction sites. Microalgae act as biocatalyst for the photosynthetic conversion of flue gas CO_2 to hydrocarbons or biofuels. Enzyme based hollow fiber contained liquid membranes and carbonanic anhydrase membranes from various microbial sources predict higher efficiency in CO_2 sequestration. Strategies for CO_2 fixation include solar energy capture; carbonic anhydrase enzymes, carbon assimilation and detoxification of soils by employing algae to remove heavy metal contaminants. New possibilities exist in bio-fixation of CO_2 from industrial waste gases through microbial and micro-algae processes, and development of nano-material compositions. The process efficiencies are however low.

Enhanced biological CO_2 capture is possible by increasing the rate of photosynthesis in photo-bioreactors. It is proposed to construct open and closed photo-bioreactors. Open bioreactors are large ponds of 10 x 10 km and 150 m deep conceived to develop new stains of micro-organisms, which can grow faster than normal rate of photosynthesis. The CO_2 introduced as bubbles is made to reach algae in shaded areas. Such ponds can produce liquid (lipid) fuel, which can be converted to biodiesel. The advantage of this method is that it does not require pure CO_2 and saves on cost of capture as well as compression. Solar bioreactor has been proposed for warm and sunny climatic regions (Stewart and Hessami, 2005). It combines solar energy use through a fibre optic system to stimulate the growth of biological organisms. The efficiencies are low because of non-uniform distribution of light throughout the bioreactor. Triangular Air-lift bioreactor has been designed to obtain experimental data for two different algal species. In a pilot-scale unit supplied with flue gases from a small power plant, removal efficiency of CO_2 was seen to be 80 per cent. Preliminary cost analysis suggested that micro algae biofixation from a 550 MW coal-fired power plant could sequester 25 per cent of the CO_2 cost-effectively, if the value recovered from the harvested algae could be priced at approximately $100 per ton. Membrane photo bioreactor technology has been reported to have potential to increase CO_2 fixation rate significantly using algal biomass.

Genome analysis of green algae has uncovered hundreds of genes associated with CO_2 capture. Photo-autotrophic organisms ranging from bacterial to higher plants have been evolved as unique Carbon Concentrating Mechanisms (CCMs). Besides enhanced CO_2 capture, genetic manipulation of crop plants by engineering C_4 genes into C_3 plants could lead to C_4 like environment in them and help to achieve optimal crop yield under predicted global climate change (Reddy et al, 2010).

5.3 Ocean geochemical fertilization

In a natural course oceans absorb and emit large quantity of CO_2 and there is no net exchange of CO_2 between the oceans and atmosphere. But as a result of anthropogenic built up of CO_2 in the atmosphere, a net flow of CO_2 from atmosphere to the upper layers of ocean is estimated to be 2 Bt/year. It is estimated that ocean can take up to 400 Bt of CO_2. The CO_2 can be dispersed on the sea surface as dry ice. The CO_2 is soluble in ocean water and its sequestration efficiency in ocean is determined from how long the gas will remain in the ocean before returning to the atmosphere. The ocean waters as active media for CO_2 storage are however, not preferred because of their prominent role in *carbon cycle* and threat of increasing CO_2 to the survival of marine species.

Geo-engineering approach of sprinkling iron would stimulated the growth of phytoplankton in the areas of deficit, sinking of organic matter and ultimate CO_2 sequestration in deep sea sediments (Lempitt et al, 2008). Various side effects of Ocean Iron Fertilization (OIF) can however occur such as fate of planktons, ration of iron to be added to CO_2 sequestered need monitoring and verification studies. First feasibility study reported in the Southern Ocean Iron Experiment (SOFeX) suggested 900 tons of carbon sequestered for 1.26 tons of iron added. Long-term CO_2 sequestration effect was not understood (Zeebe and Archer, 2005). The contamination from other trace gases on air-sea fluxes is also not identified (Sarma, 2010). To experimentally test efficacy of iron fertilization in Southern Ocean for CO_2 sequestration an experiment has been conducted in 2009 jointly by Alfred Wegener Institute, Germany and National Institute of Oceanography, India as LOHAFEX (LOHA - iron, FEX - Fertilization EXperiment).

The concentration disposal in deep oceans has been proposed (Sorai and Ohosumi, 2005) to inject liquid CO_2 at a depth greater than 3,000 m below sea level. At this depth, density of CO_2 exceeds the density of sea water. It sinks to the bottom and stays there, leading to formation of relatively immobile CO_2 hydrates or dry ice, also known as Chlatharets. The CO_2 hydrate (CO_2 -nH_2O, C > n ~ 6 or 7) have density of 1.04 - 1.07 g/cm^3. It is thus captured as a stable entity, at the temperatures below 10°C and pressure of 44.5 atmospheres (Elwell and Grant 2006). Possibilities of storage of CO_2 below permafrost layers to form gas hydrates /CO_2 Clatharets are also being investigated (Prasad, 2010).

5.4 Biochar

Biochar addition to soil to enhance CO_2 absorption capacity involves photosynthetic carbon capture by crop biomass, which is thermally decomposed in the absence of oxygen to biochar. In addition the soil fertility is expected to enhance. Life cycle assessment of different biochar systems has been carried out (Roberts, 2010). Crop yield may increase up to 10%. Economic viability of pyrolysis-biochar depends on the cost of feedstock production, pyrolysis and value of carbon credits. The energy balance studies are also reported (Gaunt and Laehman, 2008).

Farm waste through pyrolysis can be used to produce biodiesel and it can sequester carbon dioxide as well. Low temperature slow pyrolysis ofFers an energetically efficient strategy for bio-energy production and land addition of black carbon material as biochar reduces emissions to a great extent than when biochar is used only to effect emissions. Benefits of biochar returned to soil are many, it leads to (i) long-term carbon sequestration (ii) renewable energy generation (iii) biochar as a soil amendment and (iv) biomass waste management. However, many uncertainties remain and further research is needed to understand these CO_2-biochar-soil-plant interactions.

6. International policy perspectives – networking

In an international perspective, networking / collaboration is an important aspect of CCS research. The CO_2 GeoNet presented a Network of Excellence having thirteen partner countries with a common aim to integrate CO_2 storage research between the network members (Christian et al, 2008). This multi-national project has many priorities research areas, viz., predictive modeling experiments, enhanced hydrocarbon recovery, monitoring & verification, risks analysis and geological modeling. Predictive modeling studies have been developed for the sub-surface movement of CO_2 for many years into the future. Joint activities have been carried out between networking partners to form durable `virtual' and unique research centers within Europe to fulfill the need for creation of infrastructure for CCS research and providing knowledge support to policy makers.

Worldwide fossil fuels are having 85% share in total energy consumed contributing to two third of global CO_2 emissions. Carbon Sequestration Leadership Founder (CSLF) began in 2003 as multi-country initiative of Department of Energy, USA. The CSLF Technical Roadmap addresses to individual technical issues and suggest the pathways toward commercial deployment of CCS technology. It aims to collaborate on development of improved cost-effective technologies for the separation and capture of CO_2 for its transport and long-term storage. India became a founder member to CSLF in 2003 among 16 other countries. Research capabilities in India have been developed in CO_2 capture materials, lithium silicate nano-particles and membrane technology.

Multiplicity of data and role of multiple organizations has been highlighted in storage projects. The CO_2 Sequestration Initiative, a multi-national programme at Pacific Northwest National Laboratory, USA having two main components; (i) In situ Supercritical Suite (IS^3), (ii) Geological sequestration software suit (GS^3), is another step in this direction. It integrates in-situ supercritical suite IS^3 in an investigative approach to probe geochemical reactions under supercritical pressures and temperatures. It uses advanced techniques of optical spectroscopy, nuclear magnetic resonance, atomic force microscopy and high pressure XRD instruments to study supercritical CO_2 geochemistry of the cap rock and monitoring of boreholes (Murphy et al, 2010). Geological sequestration software suit GS^3 has been designed for modeling of geological sites for sequestration using advance scientific programming and benchmarking of scientific simulators for different geo-environment. In collaborative R&D mode this initiative aims at advancing our scientific knowledge of both aqueous and supercritical CO2 in the subsurface and incorporating this knowledge into simulators that are used to assess the performance of storage reservoirs. More such scientific investigations if conducted for enhanced oil recovery and enhanced coal bed methane can lead not only to additional fuels, but also to better understanding of earth processes.

International Energy Agency has been taking lead in developing policy guidelines for CCS projects and bench marking of storage projects. A Global Institute of Carbon Capture and Storage (GCCSI) has come up in Australia to provide thrust towards research and demonstration of industrial scale projects on CCS technology.

7. Conclusions

Various international initiatives in abatement of greenhouse gas emissions and recent developments towards implementation of Carbon Capture and Storage (CCS) technology are geared to achieve the sustainable energy development in fossil fuel based economies. This article describes developments in CO_2 capture technologies, various options of pre-combustion and post combustion CO_2 capture processes and underground CO_2 storage. The CCS technology is developing but not proven. Each of the options for CO_2 capture, disposal and storage in closed or open reservoirs has some unresolved challenges. There are no full-scale plants in operation of CO_2 capture yet. Increasing geo-modelling research is being carried out to prove the feasibility in large-scale operations and address the issues about permanency of CO_2 storage as well as environment safety. The R&D challenges with respect to CO_2 injection, reaction with the fluid and monitoring of transport in reservoir for CO_2 sequestration form an important part of such assessment. More attention is also required to be given to development of cost-effective geo-engineering approaches, which aim to accelerate the natural process of CO_2 absorption in the biosphere, lithosphere and in the oceans.

8. Acknowledgements

The author expressed her thanks to Chairman, Center for Studies in Science Policy and Dean, School of Social Sciences, Jawaharlal Nehru University for the encouragement. The financial support from, Council of Scientific & Industrial Research is gratefully acknowledged. The views expressed need not necessarily represent these organizations.

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Paths to Sustainable Energy
Edited by Dr Artie Ng

ISBN 978-953-307-401-6
Hard cover, 664 pages
Publisher InTech

Published in print edition November, 2010

The world's reliance on existing sources of energy and their associated detrimental impacts on the environment- whether related to poor air or water quality or scarcity, impacts on sensitive ecosystems and forests and land use - have been well documented and articulated over the last three decades. What is needed by the world is a set of credible energy solutions that would lead us to a balance between economic growth and a sustainable environment. This book provides an open platform to establish and share knowledge developed by scholars, scientists and engineers from all over the world about various viable paths to a future of sustainable energy. It has collected a number of intellectually stimulating articles that address issues ranging from public policy formulation to technological innovations for enhancing the development of sustainable energy systems. It will appeal to stakeholders seeking guidance to pursue the paths to sustainable energy.

How to reference

Malti Goel (2010). Carbon Capture and Storage Technology for Sustainable Energy, Paths to Sustainable Energy, Dr Artie Ng (Ed.), ISBN: 978-953-307-401-6, InTech, Available from: http://www.intechopen.com/books/paths-to-sustainable-energy/carbon-capture-and-storage-technology-for-sustainable-energy-

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Phone: +385 (51) 770 447
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InTech China
Unit 405, Office Block, Hotel Equatorial Shanghai
No.65, Yan An Road (West), Shanghai, 200040, China
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821