Juthika Das
School of Oceanographic Studies, Jadavpur University, kolkata700032

ShrinwantuRaha
School of Oceanographic Studies, Jadavpur University, Kolkata700032

CO₂ removal from the atmosphere by different anthropogenic methods

Juthika Das, ShrinwantuRaha

Abstract
The world is faced with an intrinsic environmental responsibility, i.e. the minimization of greenhouse gas emission to acceptable levels. This article tries to explain the methods of carbon dioxide capture and sequestration and to discuss a line of research that may, in future, help to reduce the greenhouse effect in a sustainable manner. The capture of carbon dioxide produced by combustion of fossil fuels used in electric generation can be achieved by amine scrubbing of the flue gases. This process is costly and may in the future be replaced by options such as membrane separation, molecular sieves or desiccant adsorption. Short term options of sequestration by direct injection into geologic or oceanic sinks are recognized as methods to reduce the CO_2 levels but do not addresses issues of sustainability. For this purpose, the topic of photosynthetic reactions, has long been known and examined as a natural process that can produce useful byproducts of biomass, oxygen and hydrogen and can fix carbon dioxide. In a controlled environment, such as a bio-reactor, micro-organisms capable of photosynthetic reactions may hold the key to reduce emissions in both economically and environmentally sustainable manner.

Keywords: Membrane, anthropogenic, scrubbing, oil recovery.

1. Introduction
Carbon dioxide makes up 68% of the estimated total greenhouse gas emissions (Harrington and Foster, 1999) [13], thus removal of CO2 from atmosphere is of paramount importance in ensuring our commitment in preserving the environment. Most options for the disposal of carbon dioxide may be seen as short sighted (Stewart and Hessami, 2005) [34]. The concept behind most disposal method is to offset the immediate effect on the level of CO2 in the atmosphere by relocation, i.e., by injection into either geologic or oceanic sinks (Bopp *et al*, 2003) [3]. Other, more practical, forms of disposal are currently viewed as too limited in applications or economically too expensive to justify. In a study, three major options were identified in relation to fossil fuels. They were:1) improving the efficiency of energy production, 2) reducingthe carbon content of fuels 3) sequestration of CO2 from flue gases.
Along with desiccant adsorption, geologic injection, iron fertilization at high nitrate, low chlorophyll (HNLC) area in ocean is a familiar enigma in oceanography (Chisolm *et al*., 1991) [7]. The availability of iron limits the primary productivity and thus associates uptake of carbon over large areas of the ocean (Sigman and Watson, 2000) [31]. Iron thus plays an important role in carbon cycle, and changes its supply in the surface ocean may have had a significant effect on atmospheric carbon dioxide concentration over glacial-inter-glacial cycle (Martin, 1994) [24].

2. Need for Anthropogenically Driven C Sequestration
The objective of an anthropogenically driven C sequestration process is to balance the global C budget such that future economic growth is based on a 'C-neutral' strategy of no net gain in atmospheric C -pool (Fan *et al*, 1998) [9]. Such a strategy would necessitate sequestering almost all anthropogenically generated CO2 through safe, environmentally acceptable and stable techniques with low risks of leakage. Lackner (2003) [22] estimated that if a carbon neutral strategy is based on sequestration rather than emission reduction, total C storage during the twenty first century will exceed 600 Pg with residence time of centuries to millennia. However even a leakage of 2-3 PgC yr-1 from the carbons sequestered in one of

Correspondence
ShrinwantuRaha
School of Oceanographic Studies, Jadavpur University, Kolkata700032

the pools can adversely impact the strategic planning for future generations(Pacala and Socolow, 2004) [28]. There are several technological options for the sequestration of atmospheric CO_2 into one of the other global pools. The choice of one or a combination of several techniques is important for the formulation of energy policies for future economic growth and development at national and global scales.

3. Options for Capture and Sequestration

The total amount of carbon on Earth is constant and its distribution among lithosphere, atmosphere and biosphere was relatively balanced until the advent of era of industrialized civilization. There are three options to reduce the total CO_2 emissions in atmosphere, i.e. to reduce energy intensity, to reduce carbon intensity and to enhance the sequestration of CO_2; the first option requires efficient use of energy, the second option requires switching to use non-fossil fuels such as hydrogen and renewable energy and the third option involves the development of technologies to capture and sequester more CO_2 (Hongqun et al, 2008) [18]. To enhance the sequestration of CO_2, options are sought to accelerate the fixation of carbon in lithosphere and biosphere, either CO_2 fixation by the enhancement of natural sinking process, such as forestation, ocean fertilization and many researchers have targeted at improving the current technologies or developing new approaches of CO_2 separation and capture.

3.1 MEA scrubbing process

There exists a commercial process whereby carbon dioxide is scrubbed from the flue gases of the combustion process. A chemical absorption process is used with monoethanolamine (MEA) solvent. The process allows the MEA solution to come into contact with the flue gases and mix in the absorber. The carbon dioxide rich MEA solution is sent to a stripper where it is reheated to release almost pure carbon dioxide. This carbon dioxide can be used for industrial processes or to supply the needs of a photo-bioreactor system. The MEA solution is then recycled to the absorber. This process is generally deemed as uneconomic as it results large equipment sizes and high regeneration energy requirements (Herzog et al, 2001a) [16]. Other technologies have been considered, such as membrane separation, cryogenic fractionation and adsorption using molecular sieve, but they are less energy efficient as to be considered economically viable (Herzog et al, 2001a) [16].

3.2. Membrane technology

The principle behind membrane technology could be used to assist the carbon dioxide capture process in coal combusting power plants. Motivated in part by carbon taxes imposed by an international engineering and construction group, identified an useful application using membrane technology to improve the aforementioned absorber and stripper processes. The benefit of using membrane technology was to increase the mass transfer area of a given volume, and to avoid problems associated with the vapour-liquid contact surfaces. In this application, membrane did not serve the function of separation of CO_2 from other flue gases. The separation process was still performed by the amine. For most membrane type, the amine either destroyed or wetted the surface, causing blockage. Only thep-di (tetrafluoroethylene) (PTFE) membrane type was successful.

The benefits of the membrane contactor included reduction in the installation and operating cost by 30-40% and allowed further cost reductions on the energy requirements, normally reserved to optimize the amine solution (Herzog, 2000) [15]. In this process Patil (Patil, et al. 2002) [29] explained a way to regenerate the cleaning solvent, Sc-CO_2 used in the dry cleaning process. Sc-CO_2 was used to replace traditional solvents, such as perchloroethylene and CFC113, which were considered more dangerous and environmentally damaging. The objective is to force the molecules of Sc-CO_2 through the membrane at a pressure less than 10bar and to have a permeability rate of more than 10kg/sq.m h bar and a recovery rate of 90%. For this particular design, the molecular cut off rate would need to be in range of 200-1000Dalton to allow the Sc-CO_2 to be isolated from the main stream.

3.3 Desiccant Adsorption

Ishibashi et al. (Ishibashi, 1996) [19] described a process referred to as Pressure and Temperature Swing Adsorption (PTSA) that may be applied to electric power plant flue gases. Using zeolite as desiccant, carbon dioxide can be adsorbed at normal pressure. As the adsorbent is heated, carbon dioxide is regenerated under depressurization. Further regenerative capacity and power reductions can be achieved with a moderate temperature swing. A temperature regeneration range of (50-100) °C was found to be effective. A problem with this process was found to be the reaction of the desiccant with SO_X of the flue gases. Carbon dioxide recovery was also attempted in a dehumidifier of the test pilot plant using alumina as the desiccant. The desorbed gas was fed back into the inlet of the pilot plant for an improvement in terms of system configuration. This resulted in an overall reduction in power consumption of 3%. In the overall test results, target removal efficiencies of (90-99) % purity of CO_2 were achieved.

4. Disposal Option by Direct Injection

Direct injection of carbon dioxide refers to the process whereby the gas to be sequestered is pumped into a sink usually capable of holding many mega tonnes gas over a period of time. It is recognized that most of the sinks will leak sequestered gas over a period of time, but it is still necessary to remove carbon dioxide from atmosphere to reduce the otherwise inevitable temperature rise due to the greenhouse effect. There have been two major injection options identified:

(a) Injection into the geologic reservoir
(b) Injection into the ocean.

4.1 Geologic Injection

Geologic injection may be superior to oceanic injection due to its higher expected retention rate. Expected residence times are at least thousands of years compared to that of oceanic injection of only hundreds of years. Even longer residence time could be achieved if the carbon dioxide reacted underground to form carbonate minerals, thus reducing the possibility of escape into the atmosphere (Herzog, et al 2001b) [17]. The consideration of carbon edits should be made on the retention ability of the geologic reservoir. The amount of carbon dioxide that leaks into the atmosphere should be considered as the difference of amount sequestered in the geologic formation versus the actual quantity remaining (Caldeira et al, 1996) [6]. In terms of

Australia's current direction, the GEODISC research program has been initiated by the government with the objective of addressing the key technical, commercial and environmental issues associated with geological sequestration of carbon. The first phase of this project is to identify geologic formations with the most appropriate parameters to sequester large quantities of carbon dioxide. The second phase will examine water-CO_2-rock interactions, detailed economic modeling for CO_2 transportation, compression and injection, technology for monitoring CO_2 injection levels and environmental and safety issues (Rigg, *et al*, 2001) [30].

4.1.1 Enhanced Oil Recovery (EOR)
When carbon dioxide is injected into an oil reservoir, the gas becomes miscible with the oil and promotes movement of the oil through the rock reservoir and out of the wells. As the carbon dioxide pushed with this oil, it is recaptured and re injected until as much oil as is feasible has been extracted. For each barrel of oil produced, in considering the cost of carbon dioxide and the price of oil, the idea is to add about 5-10 thousand cubic feet of carbon dioxide by a stream of cycling gas. Generally, the economic viability of EOR project depends on the price of oil and proximity of a relatively pure carbon dioxide flood source (Lake, 1989) [22]. A major reason for the lack of economic viability of EOR is the high cost of the CO_2 removal process which requires the large amount of energy. Using cogenerating techniques, by placing a combined cycle/CO_2 recovery plant in an EOR field, the problem of transportation cost can be resolved.

4.1.2 Coal Seams
Another form of geologic injection that could be considered is the use of abandoned, uneconomic coal seams. Carbon dioxide diffuses through the pore structure of coal and is physically adsorbed, thus retention in a permanent basin is possible. Coal beds often contain large number of methane. The extraction of methane could represent a value added process. Tests have shown that by using carbon dioxide instead of water to flood the bed, there exists a higher potential to recover the methane efficiently and also sequester the carbon dioxide. While this sounds ideal, much further research is needed in this area to understand and optimize the process. World-wide storage capabilities for carbon dioxide within deep coal beds are estimated to be up to 150Gt (Beecy, 2001) [2].

4.2 Oceanic Injection
The ocean contains an estimated 40,000Gt of Carbon, whereas the atmosphere and the terrestrial biosphere contains as estimated 750 and 2200Gt respectively. A doubling in the carbon concentration levels in atmosphere, therefore, represents only enough carbon to increase the ocean's concentration level by about 2%. Over a period of hundred years, it is estimated that around 80% of today's anthropogenic emission of carbon dioxide will be absorbed by the ocean. By direct injection into the ocean, this natural process is effectively enhanced, thus reducing the peak atmospheric carbon dioxide concentration and their rate of increase (Herzog, 2001$_b$) [17]. However using this method, it is estimated that around 15-20% of the carbon dioxide injected into the ocean will leach back into the atmosphere over hundreds of years. Furthermore, direct oceanic injection has unique environmental concerns. It is known that a higher

concentration of carbon dioxide decrease the level of pH of surrounding areas. Dispersing of 200years of current emissions or 1300Gt of carbon, into the ocean would decrease the average ocean pH by around 0.3units (Herzog, 2001$_b$) [17]. The deep sea pH is expected to decrease as much as 0.5pH units (Beecy, 2001) [2]. This would principally affect non-swimming marine organisms, such as zooplankton, bacteria and benthos, at depth of 1000m or more. Experimental data suggests that the problem of pH change can be avoided by using dispersal techniques during injection. Nematodes and bacteria are expected to be affected severely at pH 5.5 or 6 or less (Lake, 1989) [22]. In order to avoid the leakage of greater than 20%, injection depth should be greater than 1000m, which is around the location of thermocline. This would minimize leakage by inhibiting vertical mixing. By improving vertical dispersion of carbon dioxide, the impacts of pH can be minimized, both locally and globally. Model Theory suggests that injection at a depth of 1500m will be sensitive to location, whereas injection at a depth greater than 3000m is relatively insensitive to location. There have been a number of injection techniques suggested in order to dissolve the carbon dioxide into the ocean. These are:

(i) Droplet plume: liquid CO_2 injected from a manifold below 1000m, forming a rising plume.
(ii) Dense plume: dense CO_2 seawater mix that sinks, injected at a depth between 500-1000m.
(iii) Dry ice: dropped off a boat and allowed to sink and diffuse.
(iv) Towed pipe: injected from a boat at a depth of 1000m, forming a rising plume.
(v) CO_2 Lake: injection at a depth of around 4000m to form a stable "deep lake".

In short term the droplet and towed pipe methods are probably the most viable due to technological and economic reasons. It is also suggested that injection at 900m would avoid 90% of the global warming costs, whereas injection at 1700m deep would avoid more than 99% of the global warming costs.

5. Oceanic Fertilization
Oceanic injection can be further enhanced through a method of marine fertilization, thus enhancing the biological carbon uptake. Carbon is absorbed by photosynthetic organisms where organic matter is broken down by bacteria into inorganic compounds through a process called demineralization. Small scale fertilization experiments using iron have been conducted, but scientific research suggests that this method of sequestration has limited potential, high cost and a high level of uncertainty (Brewer PG *et al*) [4]. In a 10×10km^2 patch of ocean, the micro-nutrient Fe was added to seawater to increase the natural concentrations, the result was dramatic. There was a 30times increase in chlorophyll over the course of the experiment. And the plankton biomass increased by an order of large magnitude. This translates to100, 000kg of carbon that was fixed (Martin *et al*, 1994) [24]. Some drawbacks in the fertilization method include; changes in plankton structures which can have long term effects on the ocean ecosystem. Some climate experts suggest that there may be positive feedback from large scale iron fertilization as large quantities of sinking organic mass can trigger the production of methane gas. This would counteract the beneficial effect of carbon fixation (Graeber, 2000) [12].

5.1 Biogeochemical Changes Occurring Due To Ocean Iron Fertilization

5.1.1 Oxygen Depletion

The evolution and decline of a phytoplankton bloom is likely to increase O_2 demand in the underlying waters due to the consumption and degradation of organic matter. A decrease in O_2 concentration can lead to increase in anoxic bacterial processes such as denitrification, sulfate reduction and methanogenesis, the latter of which could lead to additional release of methane from the ocean. Model predictions have indicated the potential for O_2 to decline in the subsurface ocean as a result of fertilization. The extent of such hypoxia would be dependent on the duration of fertilization. The intensity of productivity induced the extent of sinking and the depth distribution of the decaying organic matter.

5.1.2 Change in Nutrient Concentration

Observations have shown that iron alters the uptake ratio of nitrate and silicate at very low levels. It is caused by the differing reproduction rates of phytoplankton and zooplankton communities, and an increase in nitrate uptake rates relative to silica. The shift in ratios of N: P or N: Si and phytoplankton community structure may create an imbalance in production and consumption at larger tropic levels. Some models have predicted that southern ocean fertilization would change patterns of primary productivity globally by reducing the availability of N and P in the equatorial Pacific. Increased surface nutrient depletion in areas where deep water is formed can lower the concentration of preformed nutrients in the sinking water masses. Thus, the reduction of nutrients in surface waters could re-emerge to challenge the sustainability of future primary productivity, thousands of kilometers away from the fertilized site and many years after experimentation, as deeper waters recirculate to the surface layer. Aumont and Bopp (2006) [1] and Zahariev et al. (2008) [37] all indicate a reduction in primary production and in biological export of carbon on the multi-decadral to century timescale, due to the reduction in available micronutrients returning to the surface ocean, which could represent a significant reduction in harvestable marine resources.

5.2 Production of Climate-Active Gases

5.2.1 N₂O: The production of trace gases such as N_2O is influenced by the remineralization of sinking particulate matter during the phytoplankton bloom decline and export phase, & as such responds to ocean fertilization on large temporal and spatial scales. Elevated mid-water remineralization & O_2 consumption as observed during the fate of induced phytoplankton blooms supports accelerated nitrogen cycling & N_2O production. N_2O produced is ultimately ventilated to the atmosphere, where it is long lived & has a global warming potential of between 290-310 times that of CO_2 (Fuhrman, et al, 1991) [10]. N_2O is also recognized as contributing to ozone depletion.

5.2.2 CO₂: Ocean fertilization methods must account for carbon emissions generated in the process of creating reductions, "termed leakage" (e.g., fuelused to transport Fe to site), and they must also account for any greenhouse gases generated as a result of fertilization.

5.2.3 Methane: An increase in methane production, as may occur during nitrogen fertilization, may offset the benefits of CO_2 drawdown from the atmosphere. However, Kock et al.

(2008) [20] indicate that even large changes in methane production may not be a problem in this context, emissions of methane would have to increase by 16 Tg methane yr^{-1} to offset 20% of a 0.5 Gt C yr^{-1} carbon sequestration. This is well over 10x the estimated marine source of methane to the atmosphere.

5.2.4 Other Gases: Ocean fertilization may also influence the production of volatile methyl halides (CH_3Br, CH_3I, CH_3Cl). These compounds photolyze to produce reactive halogens which are believed to contribute to depletion of stratospheric ozone (Vogt, et al, 1996) [35].

5.3 Side-Effects of Ocean Iron Fertilization–Ocean Acidification

The oceans are naturally alkaline, with an average pH of 8.2. The uptake of anthropogenic carbon since 1750 has led to the ocean becoming more acidic with an average decrease in pH which equals an increase of 30% hydrogen ions (Nelleman et al, 2008) [26]. The continued increase in atmospheric CO_2 concentrations will reduce ocean pH further in the forthcoming decades, influencing the depth distribution of remineralisation back to DIC, and reducing biocalcification in shells, bones and skeletons of marine organisms, which could result in potentially severe ecological changes. Initial estimations indicate that the southern ocean & Subarctic pacific oceans will become under saturated with respect to aragonite by 2100 (Orr et al, 2005) [27]. However, new models show that certain parts of the Arctic Ocean will be under saturated as early as 2016 (Steinacher, M., et al. 2009) [33]. Ocean fertilization activities which seek to intentionally increase the amount of CO_2 stored within the ocean have the potential to accelerate ocean acidification, with significant and unforeseen feedbacks for ocean ecosystems and the global community.

6. A Photosynthetic Solution for Co₂ Fixation

This concept suggests the photosynthetic conversion to fix carbon dioxide using bacteria or micro-organism under a controlled environment. It is a system that combines solar energy collection and a fibred optic light delivery system to stimulate biological organisms in a bio-generator to produce useful byproducts from CO_2 and other species. Cyanobacteria or micro algae have been suggested to perform the role of photosynthesis. In order to promote uniform growth of the organisms, distribution of the photosynthetic photon flux light in the wavelength range of 400-700nm needs to be delivered to the bioreactor. Beer's law suggests that a particulate laden flue gas would result in large loss of photon flux due to scattering. The efficient distribution of light throughout the photo bioreactor will affect the CO_2 uptake rates. This needs to be further investigated in order to achieve optimal growth rates for this microorganisms. The photo bioreactor system makes use of the natural process known as photosynthesis to convert light, heat and CO_2 to useful products, carbohydrates and oxygen.$6CO_2 (aq) + 6H_2O(l) + light + heat \rightarrow C_6H_{12}O_6 (aq) + 6O_2(g)$.

7. Economic and Environmental Concerns Related To the Discussed Methods

(i) MEA scrubbing process is less usual and uneconomic also because it needs large sized equipments and high regeneration energy and so this method is generally avoided.

(ii)In case of membrane technology, membrane did not serve the function of separation of CO_2 from other flue gases. The separation process was still performed by the amine. For most membrane type, the amine either destroyed or wetted the surface, causing blockage. To avoid this particular cleaning solvent has to be used.

(iii)The economic viability of EOR projects depend on the price of oil and the proximity of carbon dioxide flood source. A major reason for lack of economic viability of EOR is the high cost of the CO_2 removal process which requires large amount of energy. Placing combined cycle/CO_2 recovery process in the EOR field, the transportation cost may be reduced but it is still acknowledged that when oil prices are low, EOR projects may still be uneconomical.

(iv) By direct oceanic injection, removal of carbon dioxide can be enhanced but it has unique environmental concerns. It causes lowering oh pH up to 0.5 units and moves towards ocean acidification. The non-swimming organisms are specially affected living below 1000m or more. Nematodes and some bacteria are unable to survive in the zone having pH less than 6.

(v) As geologic and oceanic injection only delays the release of carbon dioxide into the atmosphere, and research is limited in scope regarding the effects such actions will have on the environment. Very less research has been done in establishing the detriment of ocean fertilization may have on the fragile oceanic ecosystem. A certain increase in a particular nutrient can cause a particular growth of phytoplankton species in a havoc which is known as "phytoplankton bloom" and it stops the occurrence of other species, thus disturbing the whole ecosystem. If the bloom would toxic in nature, it damages the ecosystem as well as diversity of that area.

8. Large Scale Application of Photosynthetic Carbon Fixing Method.

The analysis and comparison of individual growth rates and carbon dioxide uptake rates under a natural day-night cycle is important when choosing the optimal microorganism for a large scale production. This is because it would not be feasible to run a large scale operation like in a solar pond with a 24 hour light supply. A small scale laboratory confined photo-bioreactor is an essential first step before any large scale applications in order to identify the organisms that are robust to environmental changes such as temperature fluctuations that would occur in a solar pond. Under laboratory conditions, tests could also be conducted to ensure that the microorganisms pose no threat to the environment or ecosystem.Assuming the carbon uptake rate of 1.5g/l/day (Marukami *et al*, 1997)[25] for the particular microorganism, *S. aquatilis* could be sustained for the natural light cycle over a 24h period, for a 4000m^3 pond, up to 2.2ktonnes of CO_2/pond/year could be sequestered from the environment. Around 6000 solar ponds capable of sequestering 2.2ktonnesCO_2/year would be needed to fill this emissions gap.

9. Conclusion

The literature review presented in this paper has discussed carbon dioxide capture techniques, such as amine scrubbing to treat flue gases from fossil fuel based electrical generators and membrane, desiccant adsorption technology also. These capture and sequestration techniques have been illustrated to be not economically feasible. The sequestering of carbon dioxide was shown to be a challenging problem. Geologic and oceanic injection techniques have been illustrated and explained to be not sustainable. The natural process of photosynthesis, which can be utilized to fix carbon dioxide and produce useful by products in a sustainable fashion, has been explained to be viable, and the use of solar energized photo bio-reactor system for carbon dioxide fixation was illustrated to be technically feasible. It has been illustrated that a 4000m^3 pond under natural daily light exposure cycle could sequester up to 2.2ktonne of CO_2 per year. The initial stage for large scale CO_2 sequestration operation would be to design a laboratory scale photo-bioreactor system. The system would make use of a natural process whereby micro organisms photosynthetically fix carbon into useful products of biomass, oxygen and hydrogen. The main components of this solar energized system are the collection, transmission and delivery of the collected light energy. In comparison to other greenhouse gas mitigation options, use of photosynthetic solution is far superior and sustainable method under economic and environmental consideration.

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