Carbon Capture and Storage from Fossil Fuel Use [1]

Howard Herzog and Dan Golomb

Massachusetts Institute of Technology
Laboratory for Energy and the Environment

Glossary

Carbon sequestration: capture and secure storage of carbon that would otherwise be emitted to or remain in the atmosphere.

Carbon sources: for this chapter, we are concerned with large stationary sources of CO_2, e.g. fossil fueled power plants, cement manufacturing, ammonia production, iron and non-ferrous metal smelters, industrial boilers, refineries, natural gas wells.

Carbon capture: the separation and entrapment of CO_2 from large stationary sources.

CO_2 storage: the injection of CO_2 into geologic or oceanic reservoirs for timescales of centuries or longer.

Concise Definition of Subject

One of the approaches for mitigating potential global climate change due to anthropogenic emissions of CO_2 and other greenhouse gases is to capture CO_2 from fossil fuel using sources, and to store it in geologic or oceanic reservoirs. The capture technologies are described, and their efficiencies, cost and energy penalties are estimated. Storage capacities and effectiveness are estimated, as well as transportation costs and possible environmental impacts.

I. INTRODUCTION

Carbon sequestration can be defined as the capture and secure storage of carbon that would otherwise be emitted to, or remain, in the atmosphere. The focus of this paper is the removal of CO_2 directly from industrial or utility plants and subsequently storing it in secure reservoirs. We call this carbon capture and storage (CCS). The rationale for carbon capture and storage is to enable the use of fossil fuels while reducing the emissions of CO_2 into the atmosphere, and thereby mitigating global climate change. The storage period should exceed the estimated peak periods of fossil fuel exploitation, so that if CO_2 re-emerges into the atmosphere, it should occur past the predicted peak in atmospheric CO_2 concentrations. Removing CO_2 from the atmosphere by increasing its uptake in soils and vegetation (e.g., afforestation) or in the ocean (e.g., iron fertilization), a form of carbon sequestration sometimes referred to as enhancing natural sinks, will only be addressed briefly.

At present, fossil fuels are the dominant source of the global primary energy demand, and will likely remain so for the rest of the century. Fossil fuels supply over 85 percent of all primary energy; the rest is made up of nuclear- and hydro-electricity, and renewable energy (commercial biomass, geothermal, wind and solar energy). Currently, non-hydro renewable energy supplies less than 1% of the global energy demand. While great efforts and investments are made by many nations to increase the share of renewable energy to the primary energy demand and to

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foster conservation and efficiency improvements of fossil fuel usage, addressing climate change concerns during the coming decades will likely require significant contributions from carbon capture and storage.

II. CARBON SOURCES

Pathways for carbon capture come from three potential sources (see Figure 1). By far the largest potential sources today are fossil fueled power plants. Power plants emit more than one-third of the CO_2 emissions worldwide. Power plants are usually built in large centralized units, typically delivering 500-1000 MW of electrical power. A 1000 MW pulverized coal fired power plant emits between 6-8 Mt/y of CO_2, an oil fired single cycle power plant about two thirds of that, and a natural gas combined cycle power plant about one half of that.

Second, several industrial processes produce highly concentrated streams of CO_2 as a byproduct. Although limited in quantity, they make a good capture target, because the captured CO_2 is integral to the total production process, resulting in relatively low incremental capture costs. For example, natural gas ensuing from the wells often contains a significant fraction of CO_2 that could be captured and stored. Other industrial processes that lend themselves to carbon capture are ammonia manufacturing, fermentation and hydrogen production (e.g., in oil refining).
Third, future opportunities for CO_2 capture may arise from producing hydrogen fuels from carbon-rich feedstocks, such as natural gas, coal, and biomass. The CO_2 byproduct would be relatively pure and the incremental costs of carbon capture would be relatively low. The hydrogen could be used in fuel cells and other hydrogen fuel based technologies, but there are major costs involved in developing a mass market and infrastructure for these new fuels.

III. CAPTURE PROCESSES

CO_2 capture processes from power production fall into three general categories: (1) flue gas separation; (2) oxy-fuel combustion in power plants; and (3) pre-combustion separation. Each of these technologies carries both an energy and economic penalty. The efficiencies and economics of several technologies will be discussed in section V.

A. Flue Gas Separation

Currently, flue gas separation and CO_2 capture is practiced at about a dozen facilities worldwide. The capture process is based on chemical absorption. The captured CO_2 is used for various industrial and commercial processes, e.g. the production of urea, foam blowing, carbonated beverages, and dry ice production. Because the captured CO_2 is used as a commercial commodity, the absorption process, while expensive, is profitable because of the price realized for the commercial CO_2.

Chemical absorption refers to a process where a gas, in our case CO_2, is absorbed in a liquid solvent by formation of a chemically bonded compound. When used in a power plant to capture CO_2, the flue gas is bubbled through the solvent in a packed absorber column, where the solvent preferentially removes the CO_2 from the flue gas. Afterward, the solvent passes through a regenerator unit where the absorbed CO_2 is stripped from the solvent by counterflowing steam at 100-120°C. Water vapor is condensed, leaving a highly concentrated (over 99%) CO_2 stream, which may be compressed for commercial utilization or storage. The lean solvent is cooled to 40-65°C, and recycled into the absorption column.

The most commonly used absorbent for CO_2 absorption is monoethanolamine (MEA). The fundamental reaction for this process is:

$$C_2H_4OHNH_2 + H_2O + CO_2 \leftrightarrow C_2H_4OHNH_3^+ + HCO_3^- \quad (1)$$

During the absorption process, the reaction proceeds from left to right; during regeneration, the reaction proceeds from right to left. The cooling and heating of the solvent, pumping and compression require power input from the power plant thermal cycle, derating the thermal efficiency (heat rate) of the power plant. A schematic of a chemical absorption process for power plant flue gas is depicted in Figure 2.

In order to reduce the capital and energy cost, and the size of the absorption and regenerator (stripper) columns, new processes are being developed. One example is the membrane-absorption process, where a microporous membrane made of polytetrafluoroethylene separates the flue gas from the solvent. The membrane allows for greater contacting area within a given volume, but by itself the membrane does not perform the separation of CO_2 from the rest of the flue gases. It is the solvent that selectively absorbs CO_2. The use of a gas membrane has several advantages: (a) high packing density; (b) high flexibility with respect to flow rates and solvent selection; (c) no foaming, channeling, entrainment and flooding – common problems in packed absorption towers; (d) the unit can be readily transported, e.g. offshore; (e) significant savings in weight.

It is possible to design a once through scrubbing process (i.e., no regeneration step). For example, one could scrub CO_2 from flue gas with seawater and then return the whole mixture to the ocean for storage. However, to-date these approaches are not as practical as those using a regenerable solvent. In the seawater scrubbing example, the large volumes of water that are required result in large pressure drops in the pipes and absorber.

Other processes have been considered to capture CO_2 from power plant and industrial boiler flue gases, e.g. membrane separation, cryogenic fractionation, and adsorption using molecular sieves. Generally, these processes are less energy efficient and more expensive than the absorption methods.

B. Oxy-Fuel Combustion

When a fossil fuel (coal, oil and natural gas) is combusted in air, the fraction of CO_2 in the flue gas ranges from 3-15%, depending on the carbon content of the fuel and the amount of excess air necessary for the combustion process. The separation of CO_2 from the rest of the flue gases (mostly N_2) by chemical or physical means is capital and energy intensive. An alternative is to burn the fossil fuel in pure or enriched oxygen. In such a fashion the flue gas will contain mostly CO_2 and H_2O. A part of the flue gas needs to be recycled into the combustion chamber in order to control the flame temperature. From the non-recycled flue gas, water vapor can be readily condensed, and the CO_2 can be compressed and piped directly to the storage site.

Of course, the separation process has now shifted from the flue gas to the intake air: one has to separate oxygen from nitrogen of the air. The air separation unit (ASU) alone may consume about 15% of a power plant's electric output, requiring a commensurate increase of fossil fuel to be consumed for achieving the rated electric output of the plant. In the ASU, air is separated into liquid oxygen, gaseous nitrogen, argon and other minor ingredients of air. The latter are saleable byproducts of the oxyfuel plant. Pilot scale studies indicate that the oxyfuel method of capturing CO_2 can be retrofitted to existing pulverized coal (PC) plants.

C. Pre-Combustion Capture

Capturing CO_2 before combustion offers some advantages. First, CO_2 is not yet diluted by the combustion air. Second, the CO_2 containing stream is usually at elevated pressure. Therefore, more efficient separation methods can be applied, e.g. using pressure-swing-absorption in physical solvents, such as methanol or polyethylene glycol (commercial brands are called Rectisol and Selexol). Pre-combustion capture is usually applied in coal gasification combined cycle (IGCC) power plants. This process includes gasifying the coal to produce a synthesis gas composed of CO and H_2; reacting the CO with water (water-gas shift reaction) to produce CO_2 and H_2; capturing the CO_2; and sending the H_2 to a turbine to produce electricity. Since the primary fuel sent to the gas turbine is now hydrogen, some can be bled off as a fuel for separate use, such as in hydrogen fuel cells to be used in transportation vehicles. One of the biggest barriers to this pathway is that currently electricity generation is cheaper in pulverized coal (PC) power plants than in IGCC plants. The pre-combustion process could be utilized when natural gas is the primary fuel. Here, a synthesis gas is formed by reacting natural gas with steam to produce CO_2 and H_2. However, it is unproven whether pre-combustion capture is preferable to the standard post-combustion capture for the case of using natural gas.

Worldwide, gasification facilities exist today that do not generate electricity, but synthesis gas and various other byproducts of coal gasification. In these facilities, CO_2 is separated after the gasification stage from the other gases, such as methane, hydrogen or a mix of carbon monoxide and hydrogen. The synthesis gas or hydrogen are used as a fuel or for chemical raw material, e.g. for liquid fuel manufacturing or ammonia synthesis. The CO_2 can also be used as a chemical raw material, for dry ice manufacturing, carbonated beverages, and enhanced oil recovery (EOR). For example, the Great Plains Synfuel Plant, near Beulah, North Dakota, gasifies 16,326 metric tons per day of lignite coal into 3.5 million standard cubic meters per day of combustible syngas, and close to 7 million standard cubic meters of CO_2. A part of the CO_2 is captured by a physical solvent based on methanol. The captured CO_2 is compressed and 2.7 million standard cubic meters per day are piped over a 325 km distance to the Weyburn, Saskatchewan, oil field, where the CO_2 is used for enhanced oil recovery.

IV. CO_2 STORAGE

Following the capture process, CO_2 needs to be stored, so that it will not be emitted into the atmosphere. Several key criteria must be applied to the storage method: (a) the storage period should be prolonged, preferably hundreds to thousands of years; (b) the cost of storage, including the cost of transportation from the source to the storage site, should be minimized; (c) the risk of accidents should be eliminated; (d) the environmental impact should be minimal; (e) the storage method should not violate any national or international laws and regulations.

Storage media include geologic sinks and the deep ocean. Geologic storage includes deep saline formations (sub-terranean and sub-seabed), depleted oil and gas reservoirs, enhanced oil recovery, and unminable coal seams. Deep ocean storage includes direct injection of liquid carbon dioxide into the water column at intermediate depths (1000-3000 m), or at depths greater than 3000 m, where liquid CO_2 becomes heavier than sea water, so it would drop to the ocean bottom and form a so-called "CO_2 lake." In addition, other storage approaches are proposed, such as enhanced uptake of CO_2 by terrestrial and oceanic biota, and mineral weathering. While the latter approaches will be discussed briefly, they refer to the uptake of CO_2 from the atmosphere, not from CO_2 that has been captured from emission sources. Finally, captured CO_2 can be used as a raw material for the chemical industry. However, the prospective amounts of CO_2 that can be utilized is but a very small fraction of CO_2 emissions from anthropogenic sources.

Table 1 lists the estimated worldwide capacities for CO_2 storage in the various media. As a comparison to the storage capacities, we note that current global anthropogenic emissions amount to close to 7 GtC per year (1 GtC = 1 billion metric tons of carbon equivalent = 3.7 Gt CO_2).

A. Geologic Storage

Geological sinks for CO_2 include depleted oil and gas reservoirs, enhanced oil recovery, unminable coal seams, and deep porous formations. Together, these can hold hundreds to thousands of gigatons of carbon (GtC), and the technology to inject CO_2 into the ground is well established. CO_2 is stored in geologic formations by a number of different trapping mechanisms, with the exact mechanism depending on the formation type.

Depleted Oil and Gas Reservoirs. Though a relatively new idea in the context of climate change mitigation, injecting CO_2 into depleted oil and gas fields has been practiced for many years. The major purpose of these injections was to disposing of "acid gas," a mixture of CO_2, H_2S and other byproducts of oil and gas exploitation and refining. In 2001, nearly 200 million cubic meters of acid gas was injected into formations across Alberta and British Columbia at more than 30 different locations. Acid gas injection has become a popular alternative to sulfur recovery and acid gas flaring, particularly in Western Canada. Essentially, acid gas injection schemes remove CO_2 and H_2S from the produced oil or gas stream, compress and transport the gases via pipeline to an injection well, and re-inject the gases into a different formation for disposal. Proponents of acid gas injection claim that these schemes result in less environmental impact than alternatives for processing and disposing unwanted gases. In most of these schemes, CO_2 represents the largest component of the acid gas, typically up to 90% of the total volume injected for disposal. Successful acid gas injection requires a nearby reservoir with sufficient porosity, amply isolated from producing reservoirs and water zones. Historically, depleted and producing reservoirs have proven to be extremely reliable containers of both hydrocarbons and acid gases over time.

Enhanced Oil Recovery. Carbon dioxide injection into geological formations for enhanced oil recovery (EOR) is a mature technology. In 2000, 84 commercial or research-level CO_2-EOR projects were operational world-wide. The United States, the technology leader, accounts for 72 of the 84 projects, most of which are located in the Permian Basin. Combined, these projects produced 200,772 barrels (bbl) of oil per day, a small but significant fraction (0.3%) of the 67.2 million bbl per day total of world-wide oil production that year. Outside the United States and Canada, CO_2 floods have been implemented in Hungary, Turkey and Trinidad.

In most CO_2-EOR projects, much of the CO_2 injected into the oil reservoir is only temporarily stored. This is because the decommissioning of an EOR project usually involves the "blowing down" of the reservoir pressure to maximize oil recovery. This blowing down results in CO_2 being released, with a small but significant amount of the injected CO_2 remaining dissolved in the immobile oil. The Weyburn Field in southeastern Saskatchewan, Canada, is the only CO_2-EOR project to date that has been monitored specifically to understand CO_2 storage. In the case of the Weyburn Field, no blow-down phase is planned, thereby allowing for permanent CO_2 storage. Over the anticipated 25-year life of the project, it is expected that the injection of some 18 million tons of CO_2 from the Dakota Gasification Facility in North Dakota will produce around 130 million bbl of enhanced oil. This has been calculated to be equivalent to approximately 14 million tons of CO_2 being prevented from reaching the atmosphere, including the CO_2 emissions from electricity generation that is required for the whole EOR operation.

Unmineable Coal Seams. Abandoned or uneconomic coal seams are another potential storage site. CO_2 diffuses through the pore structure of coal and is physically adsorbed to it. This process is similar to the way in which activated carbon removes impurities from air or water. The exposed coal surface has a preferred affinity for adsorption of CO_2 than for methane with a ratio of 2:1. Thus, CO_2 can be used to enhance the recovery of coal bed methane (CMB). In some cases, this can be very cost effective or even cost free, as the additional methane removal can offset the cost of the CO_2 storage operations. CBM production has become an increasingly important component of natural gas supply in the United States during the last decade. In 2000, approximately 40 billion standard cubic meters (scm) of CBM was produced, accounting for about 7 percent of the nation's total natural gas production. The most significant CBM production, some 85 percent of the total, occurs in the San Juan basin of southern Colorado and northern New Mexico. Another 10 percent is produced in the Black Warrior basin of Alabama, and the remaining 5 percent comes from rapidly developing Rocky Mountain coal basins, namely the Uinta basin in Utah, the Raton basin in Colorado and New Mexico, and the Powder River basin in Wyoming. Significant potential for CBM exists worldwide. A number of coal basins in Australia, Russia, China, India, Indonesia, and other countries have also been identified as having a large CBM potential. The total worldwide potential for CBM is estimated at around two trillion scm , with about 7.1 billion tons of associated CO_2 storage potential.

Deep Saline Formations. Deep saline formations, both sub-terranean and sub-seabed, may have the greatest CO_2 storage potential. These reservoirs are the most widespread and have the largest volumes. These reservoirs are very distinct from the more familiar reservoirs used for fresh water supplies. Research is currently underway in trying to understand what percentage of these deep saline formations could be suitable CO_2 storage sites.

The density of CO_2 depends on the depth of injection, which determines the ambient temperature and pressure. The CO_2 must be injected below 800 m, so that it is in a dense phase (either liquid or supercritical). When injected at these depths, the specific gravity of CO_2 ranges from 0.5 to 0.9, which is lower than that of the ambient aquifer brine. Therefore, CO_2 will naturally rise to the top of the reservoir, and a trap is needed to ensure that it does not reach the surface. Geologic traps overlying the aquifer immobilize the CO_2. In the case of aquifers with no distinct geologic traps, an impermeable cap-rock above the underground reservoir is needed. This forces the CO_2 to be entrained in the groundwater flow and is known as hydrodynamic trapping. Two other very important trapping mechanisms are solubility and mineral trapping. Solubility and mineral trapping involve the dissolution of CO_2 into fluids, and the reaction of CO_2 with minerals present in the host formation to form stable, solid compounds like carbonates. If the flow path is long enough, the CO_2 might all dissolve or become fixed by mineral reactions before it reaches the basin margin, essentially becoming permanently trapped in the reservoir.

The first, and to date only, commercial-scale project dedicated to geologic CO_2 storage is in operation at the Sleipner West gas field, operated by Statoil, located in the North Sea about 250 km off the coast of Norway. The natural gas produced at the field has a CO_2 content of about 9%. In order to meet commercial specifications, the CO_2 content must be reduced to 2.5% percent. At Sleipner, the CO_2 is compressed and injected via a single well into the Utsira Formation, a 250 m thick aquifer located at a depth of 800 m below the seabed. About one million metric tons of CO_2 have been stored annually at Sleipner since October 1996, equivalent to about 3% of Norway's total annual CO_2 emissions. A total of 20 Mt of CO_2 is expected to be stored over the lifetime of the project. One motivation for doing this was the Norwegian offshore carbon tax, which was then about $50 (USD) per metric ton of CO_2 (the tax was lowered to $38 per ton on January 1, 2000). The incremental investment cost for storage was about $80 million. Solely on the basis of carbon tax savings, the investment was paid back in about one-and-a-half years. This contrasts to most gas fields worldwide where the separated CO_2 is simply vented into the atmosphere.

Statoil is planning a second storage project involving about 0.7 Mt per year of CO_2 produced at the Snohvit gas field in the Barents Sea off northern Norway to be injected into a deep sub-sea formation.

Environmental and Safety Concerns. Fundamentally, a geologic storage system can be broken down into two general subsystems, namely operational and *in situ*. The operational subsystem is composed of the more familiar components of CO_2 capture, transportation and injection, which have been successfully deployed in the previously discussed applications. Once CO_2 is injected in the reservoir it enters an *in situ* subsystem in which the control of CO_2 is transferred to the forces of nature. Years of technological innovation and experience have given us the tools and expertise to handle and control CO_2 in the operational subsystem with adequate certainty and safety; however, that same level of expertise and understanding is largely absent once the CO_2 enters the storage reservoir. Direct environmental and human health risks are of utmost concern. As such, researchers are now conducting studies to evaluate the likelihood and potential impacts associated with leaks, slow migration and accumulation, and induced seismicity.

B. Ocean Storage

By far, the ocean represents the largest potential sink for anthropogenic CO_2. It already contains an estimated 40,000 GtC (billion metric tons of carbon) compared with only 750 GtC in the atmosphere and 2200 GtC in the terrestrial biosphere. Apart from the surface layer, deep ocean water is unsaturated with respect to CO_2. It is estimated that if all the anthropogenic CO_2 that would double the atmospheric concentration were injected into the deep ocean, it would change the ocean carbon concentration by less than 2%, and lower its pH by less than 0.15 units. Furthermore, the deep waters of the ocean are not hermetically separated from the atmosphere. Eventually, on a time scale of 1000 years, over 80% of today's anthropogenic emissions of CO_2 will be transferred to the ocean. Discharging CO_2 directly to the ocean would accelerate this ongoing but slow natural process and would reduce both peak atmospheric CO_2 concentrations and their rate of increase.

In order to understand ocean storage of CO_2, some properties of CO_2 and seawater need to be elucidated. For efficiency and economics of transport, CO_2 would be discharged in its liquid phase. If discharged above about 500 m depth, that is at a hydrostatic pressure less than 50 atm, liquid CO_2 would immediately flash into a vapor, and bubble up back into the atmosphere. Between 500 and about 3000 m, liquid CO_2 is less dense than seawater, therefore it would ascend by buoyancy. It has been shown by hydrodynamic modeling that if liquid CO_2 were released in these depths through a diffuser such that the bulk liquid breaks up into droplets less than about 1 cm in diameter, the ascending droplets would completely dissolve before rising 100 m. Because of the higher compressibility of CO_2 compared to seawater, below about 3000 m liquid CO_2 becomes denser than seawater, and if released there, would descend to greater depths. When liquid CO_2 is in contact with water at temperatures less than 10^{o}C and pressures greater than 44.4 atm, a solid hydrate is formed in which a CO_2 molecule occupies the center of a cage surrounded by water molecules. For droplets injected into seawater, only a thin film of hydrate forms around the droplets.

There are two primary methods under serious consideration for injecting CO_2 into the ocean. One involves dissolution of CO_2 at mid-depths (1500-3000 m) by injecting it from a bottom mounted pipe from shore or from a pipe towed by a moving CO_2 tanker. The other is to inject CO_2 below 3000 m, where it will form a "deep lake". Benefits of the dissolution method are that it relies on commercially available technology and the resulting plumes can be made to have high dilution to minimize any local environmental impacts due to increased CO_2 concentration or reduced pH. The concept of a CO_2 lake is based on a desire to minimize leakage to the atmosphere. Research is also looking at an alternate option of injecting the CO_2 in the form of bicarbonate ions in solution. For example, seawater could be brought into contact with flue gases in a reactor vessel at a power plant, and that CO_2-rich water could be brought into contact with crushed carbonate minerals, which would then dissolve and form bicarbonate ions. Advantages of this scheme are that only shallow injection is required (>200 m) and no pH changes will result. Drawbacks are the need for large amounts of water and carbonate minerals.

Discharging CO_2 into the deep ocean appears to elicit significant opposition, especially by some environmental groups. Often, discharging CO_2 is equated with dumping toxic materials into the ocean, ignoring that CO_2 is not toxic, that dissolved carbon dioxide and carbonates are natural ingredients of seawater, and as stated before, atmospheric CO_2 will eventually penetrate into deep water anyway. This is not to say that seawater would not be acidified by injecting CO_2. The magnitude of the impact on marine organisms depends on the extent of pH change and the duration of exposure. This impact can be mitigated by the method of CO_2 injection, e.g. dispersing the injected CO_2 by an array of diffusers, or adding pulverized limestone to the injected CO_2 in order to buffer the carbonic acid.

V. ECONOMICS

CCS costs can be considered in terms of four components: separation, compression, transport, and injection. These costs depend on many factors, including the source of the CO_2, transportation distance, and the type and characteristics of the storage reservoir. In this section, we consider costs associated with capture from fossil fuel-fired power plants with subsequent transport and storage. In this case, the cost of capture includes both separation and compression costs because both of these processes almost always occur at the power plant.

Cost of Capture. Technologies to separate and compress CO_2 from power plant flue gases exist and are commercially available. However, they have not been optimized for capture of CO_2 from a power plant for the purpose of storage. The primary difference in capturing CO_2 for commercial markets versus capturing CO_2 for storage is the role of energy. In the former case, energy is a commodity, and all we care about is its price. In the latter case, using energy generates more CO_2 emissions, which is precisely what we want to avoid. An energy penalty can be calculated as (x-y)/x, where x is the output in kW of a reference power plant without capture and y is the output in kW of the same plant with capture. The calculation requires that the same fuel input be used in both cases. For example, if the power plant output is reduced by 20% because of the capture process (y=.8x), the process is said to have an energy penalty of 20%.

We can account for the energy penalty by calculating costs on a CO_2 avoided basis. As shown in Figure 3, due to the extra energy required to capture CO_2, the amount of CO_2 emissions avoided is always less than the amount of CO_2 captured. Therefore, capturing CO_2 for purposes of storage requires more emphasis on reducing energy inputs than in traditional commercial processes.

Based on the results of major economic studies available in the literature adjusted to a common economic basis, Figure 4 summarizes the present cost of electricity (COE) from three types of CO_2 capture power plants: Integrated Gasification Combined Cycles (IGCC), Pulverized Coal Fired Single Cycle (PC), and Natural Gas Combined Cycles (NGCC). The mean and range (plus/minus one standard deviation) are shown for each capture plant, along with a typical COE for a no capture plant. This results in an increase in the cost of electricity of 1-2¢/kWh for an NGCC plant, 1-3¢/kWh for an IGCC plant, and 2-4¢/kWh for a PC plant.

The energy penalties for each of these processes have also been estimated. The energy penalty for an NGCC plant is about 16%, whereas for a PC plant it is 28%. Each of these plants use the amine solvent process (see Section III). The energy penalty for a PC plant is greater than for an NGCC plant because coal has a larger carbon content than gas. The major energy losses are associated with energy required to blow the flue gas through the amine absorption column, the heat required to strip off the CO_2 and regenerate the amine, and the energy required to compress the CO_2. The energy penalty for an IGCC plant is 14%, actually less than for a PC plant despite its use of coal. This is because the high CO_2 partial pressure in the IGCC stream allows the use of an energy efficient physical absorption process instead of the chemical absorption process. However, some of these gains are offset by the energy loss associated with converting the coal into CO_2 plus H_2.

Cost of Transport. Figure 5 shows the cost of transporting CO_2 in large quantities by pipeline. Costs can vary greatly because pipeline costs depend on terrain, population density, etc. Economies of scale are realized when dealing with over 10 million metric tons per year (equivalent to about 1500 MW of coal-fired power). This cost is about \$0.50/metric tonnne/100 km, compared to truck transport of \$6/metric tonne/100 km.

Cost of Injection and Storage. Figure 6 summarizes the cost of the various carbon storage technologies on a greenhouse gas avoided basis. The points on the graphs are for a typical base case, while the bars represent the range between representative high and low cost cases. The ranges reflect the range of conditions found in the various reservoirs (depth, permeability, etc.), distance between source and sink (a range of 0-300 km here), and by-product prices (i.e., oil and gas).

Excluding the more expensive ocean tanker option, the *typical base case costs* for CO_2 storage (transport + injection) without oil or gas by-product credit is in the range of \$3-5.50 per tonne CO_2 (\$11-20 per tonne C). The *overall cost range* can be characterized as \$2-15 per tonne CO_2 (\$7-55 per tonne C). With a by-product credit for the gas or oil, the credit will offset the storage costs in many instances. For example, in the base EOR case, one can afford to pay \$12.21 per tonne of CO_2 and still break even (i.e., the costs equal the by-product credit).

Overall Costs. Economic models of the general economy (i.e., a General Equilibrium Model) can be used to estimate the market carbon price required for adaptation of CCS technologies in the electric power industry. Carbon prices must be established through government policy, such as a tax or a cap-and-trade system. Assuming the costs and technology level outlined above, carbon prices must reach \$100/tC in order for CCS technologies to start being adopted by the power industry on a significant scale (>5% market penetration). As the carbon price increases, CCS technologies will be adapted more quickly and achieve larger market penetration.

CCS technologies can be adopted at carbon prices much less than \$100/tC. These targets of opportunity will either have very inexpensive capture costs (from non-power sources like natural gas processing, ammonia production, etc.) or be able to claim a by-product credit (e.g., EOR). All the commercial scale CO_2 storage projects either in operation (Sleipner, Weyburn) or planned (Snovit by Statoil in North Sea and In Salah by BP in Algeria) can be classified as targets of opportunity. Finally, new technologies can reduce the costs associated with CCS.

VI. ALTERNATE APPROACHES

In the previous sections we addressed the technologies for separating CO_2 from fossil fuel streams before or after combustion and storing the captured CO_2 in geologic or oceanic sinks. In this section, we briefly identify some alternative approaches that have been proposed for CO_2 capture and/or storage. The topics that we have chosen to include in this section are ones that have received significant publicity and/or funding. Their inclusion is in no way an endorsement, just as the exclusion of any approach is not a rejection. The enhanced uptake of CO_2 by the terrestrial biosphere (e.g., afforestation) is currently a subject of intensive debate, but this approach falls outside the scope of this article.

A. Capture by Microalgae

The concept is to grow algae in artificial ponds, add the necessary nutrients and fertilize the ponds with CO_2 from flue gas. Under these conditions it is possible to enhance the growth of microalgae, harvest the algal biomass and convert it to food, feed or fuel. At present, about 5000 tons of food- and feed-grade microalgae biomass are produced annually in large open pond systems. As such, this approach cannot be considered as a sequestration method because the CO_2 will be returned to the atmosphere upon digestion and respiration of the food or feed. What is even worse, when used as a feed to ruminating animals, some of the ingested carbon may be converted to methane, which is a stronger greenhouse gas than carbon dioxide. But if the biomass is converted to *biofuel* and subsequently combusted, then it replaces fossil fuel, and thus the commensurate emission of fossil fuel generated CO_2 is avoided. However, for this approach to be viable as a greenhouse gas control method, it is necessary to significantly lower the cost from today's level. Despite some intensive efforts, primarily from Japan, little progress has been made towards this goal.

B. Ocean Fertilization

It has been hypothesized that by fertilizing the ocean with limiting nutrients such as iron, the growth of marine phytoplankton will be stimulated, thus increasing the uptake of atmospheric CO_2 by the ocean. The presumption is that a portion of the phytoplankton will eventually sink to the deep ocean. Researchers have targeted "high-nutrient-low-chlorophyll" (HNLC) ocean regions, specifically the eastern Equatorial Pacific, the northeastern Subarctic Pacific, and the Southern Oceans.

Four major open ocean experiments have been conducted to test the "iron hypothesis", two in the Equatorial Pacific (IRONEX I in 1993 and IRONEX II in 1995) and two in the Southern Ocean (SOIREE in 1999 and EISENEX in 2000). These experiments, funded through basic science programs (not sequestration programs), show conclusively that phytoplankton biomass can be dramatically increased by the addition of iron. However, while a necessary condition, it is not sufficient to claim iron fertilization will be effective as a CO_2 sequestration option.
The proponents of iron fertilization claim very cost effective mitigation on the order of \$1-10/tC, but critical scientific questions remain unanswered. While iron increases uptake of CO_2 from the atmosphere to the surface ocean, it needs to be exported to the deep ocean to be effective for sequestration. No experiments have yet attempted to measure export efficiency, which is an extremely difficult value to measure (some people claim that it cannot be measured experimentally). In addition, there are concerns about the effect on ecosystems, such as inducing anoxia (oxygen depletion) and changing the composition of phytoplankton communities.

C. Mineral Storage

Several minerals found on the surface of the earth uptake CO_2 from the atmosphere with the formation of carbonates, and thus permanently storing the CO_2. Such minerals are calcium and magnesium silicates. For example, the following reaction occurs with serpentine, a magnesium silicate:

$$Mg_3Si_2O_5(OH)_4 + 3CO_2(g) = 3MgCO_3 + 2SiO_2 + 2H_2O(l)$$

While the reaction is thermodynamically favored, it is extremely slow in nature (characteristic time on the order of a hundred thousand years). The challenge is to speed up the reaction in order to be able to design an economically viable process. Many reaction pathways have been explored to varying degrees. While some have shown progress, none has yet resolved all the issues necessary to make a commercial process.

D. Non-biological Capture from Air

The terrestrial biosphere routinely removes CO_2 from air, primarily through photosynthesis. It has been suggested that CO_2 can also be removed from air via non-biological means. While some concept papers have been published, no viable methods to accomplish this goal have been proposed. The problem is that the partial pressure of CO_2 in the air is less than 0.0004 atm, compared to about 0.1 atm in flue gas and up to 20 atm in synthesis gas. The difficulty in capture increases as the partial pressure of CO_2 decreases. Therefore, one can question whether CO_2 can be captured from air with acceptable energy penalties and costs. If so, it almost surely will take development of a capture process very different from those that exist today.

E. Utilization

CO_2 from fossil fuel could be utilized as a raw material in the chemical industry for producing commercial products that are inert and long-lived, such as vulcanized rubber, polyurethane foam and polycarbonates. Only a limited amount of CO_2 can be stored in such a fashion. Estimates of the world's commercial sales for CO_2 is less than 0.1 GtC equivalent, compared to annual emissions of close to 7 GtC equivalent. It has been suggested that CO_2 could be recycled into a fuel. This would create a market on the same scale as the CO_2 emissions. However, to recycle CO_2 to a fuel would require a carbon-free energy source. If such a source existed, experience suggests that it would be more efficient and cost-effective to use that source directly to displace fossil fuels rather than to recycle CO_2.

VII. BIBLIOGRAPHY

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Table 1

The worldwide capacity of potential CO_2 storage reservoirs	
Ocean and land-based sites together contain an enormous capacity for storage of CO_2[a]. The world's oceans have by far the largest capacity for carbon storage.	
Sequestration option	Worldwide capacity[b]
Ocean	1,000 – 10,000+ GtC
Deep saline formations	100–10,000 GtC
Depleted oil and gas reservoirs	100 – 1,000 GtC
Coal seams	10–1,000 GtC
Terrestrial	10 - 100 GtC
Utilization	currently <0.1 GtC/yr

[a] Worldwide total anthropogenic carbon emissions are ~7 GtC per year (1 GtC = 1 billion metric tons of carbon equivalent).

[b] Orders of magnitude estimates.

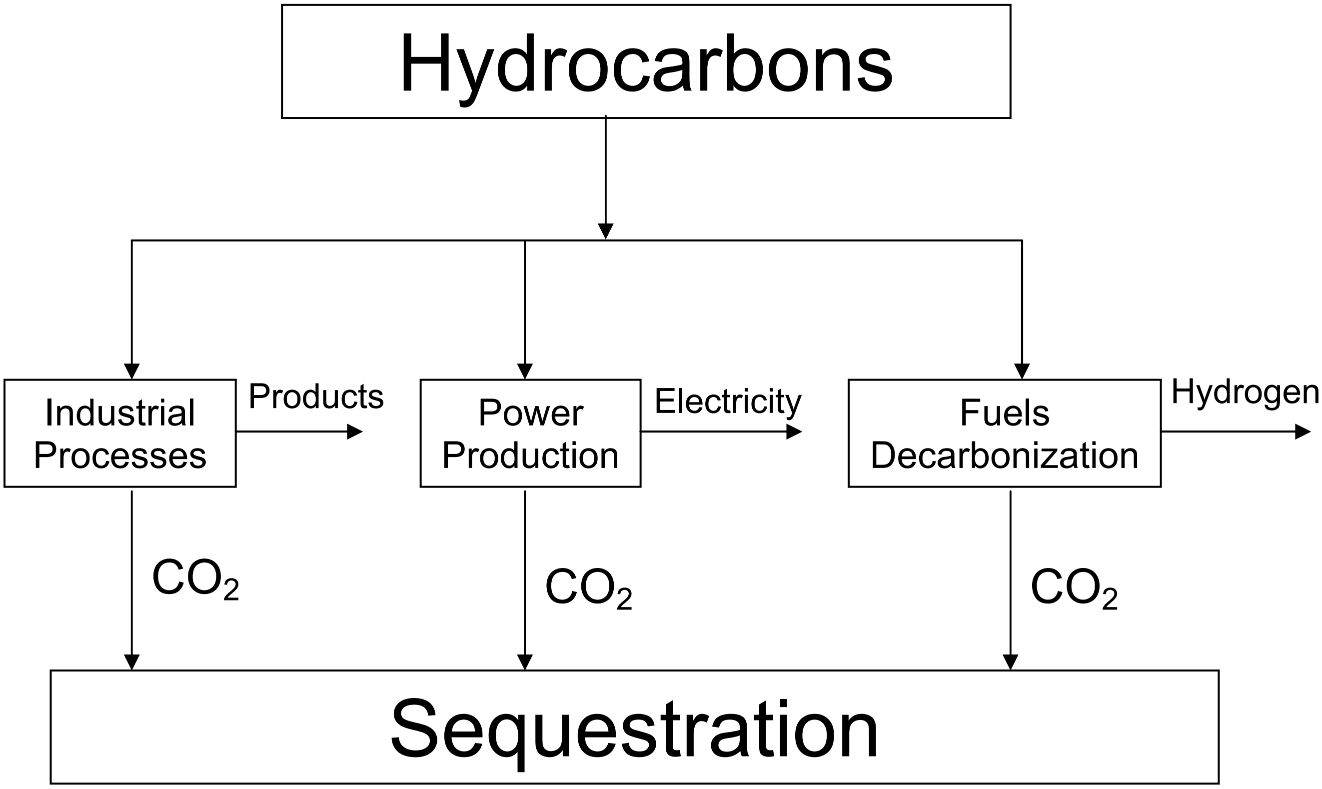

Figure 1. Sources of CO_2 for sequestration -- an industrial by-product, captured from power plants, or a by-product of future fuel decarbonization plants.

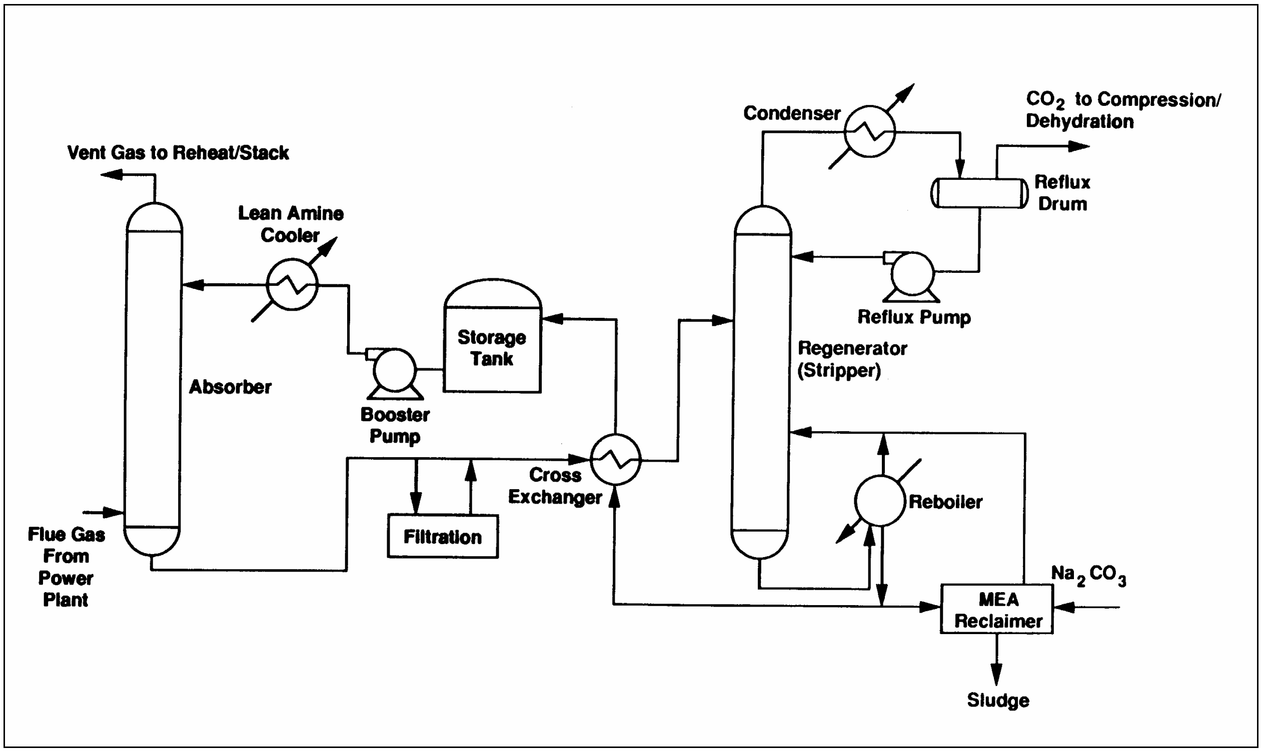

Figure 2. Process flow diagram for the amine separation process.

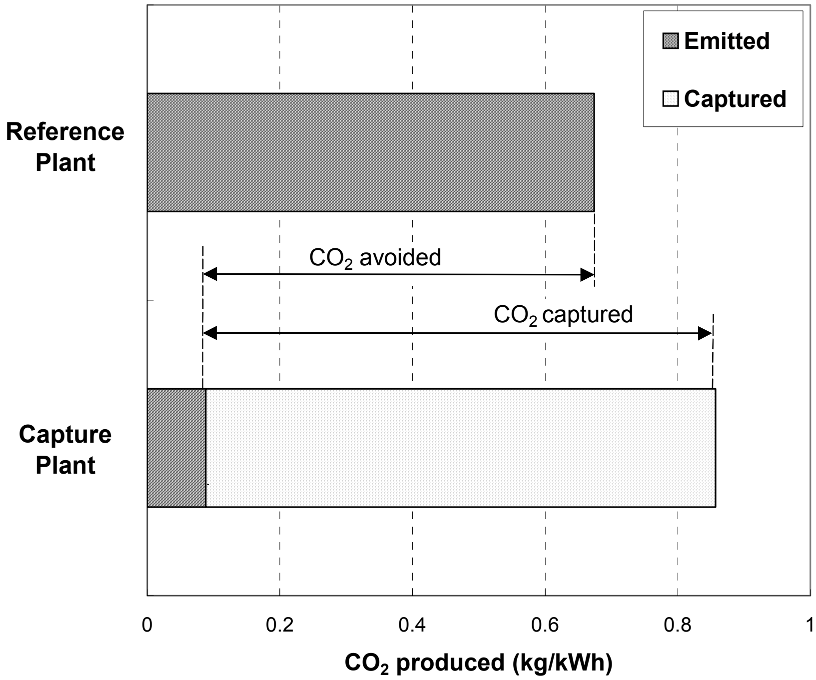

Figure 3. Graphical representation of avoided CO_2. The avoided emissions are simply the difference of the actual emissions per kWh of the two plants. Note that due to the energy penalty, the emissions avoided are always less than the captured CO_2.

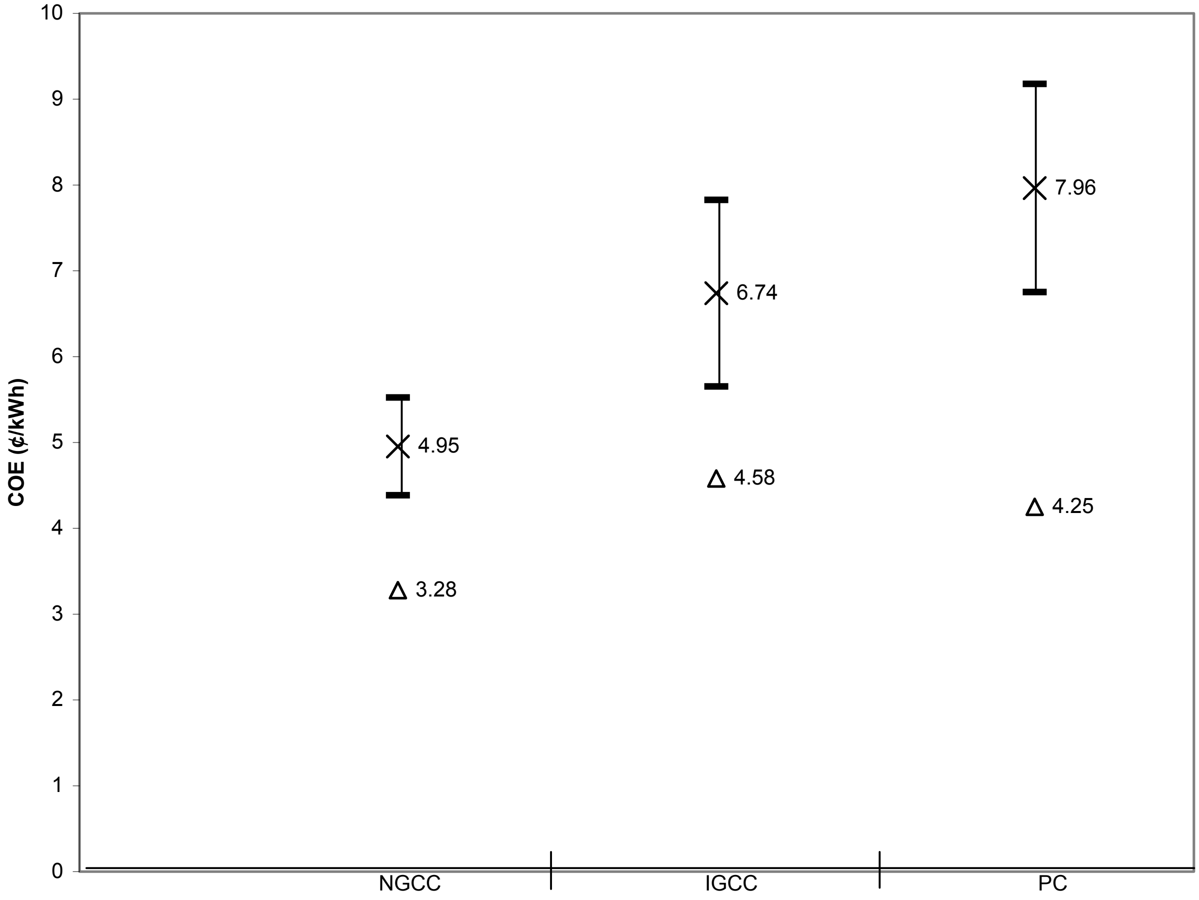

Figure 4. The cost of electricity with capture for various types of power plants (NGCC is natural gas combined cycle, IGCC is integrated coal gasification combined cycle, PC is pulverized coal). The triangles represent a reference plant with no capture. The cost of electricity for CO_2 capture plants is based on a survey of the literature and is shown as a mean and a range of one standard deviation.

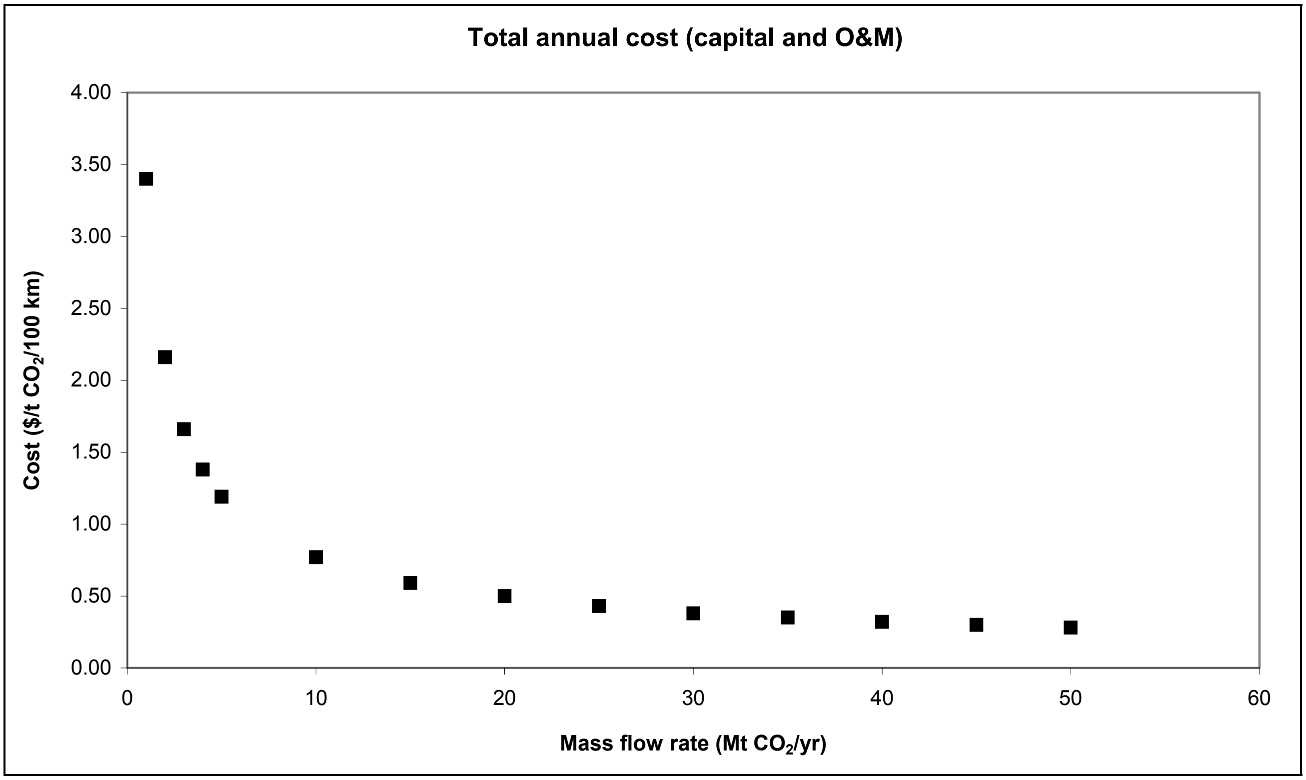

Figure 5. Cost for CO_2 transport via pipeline as a function of CO_2 mass flow rate

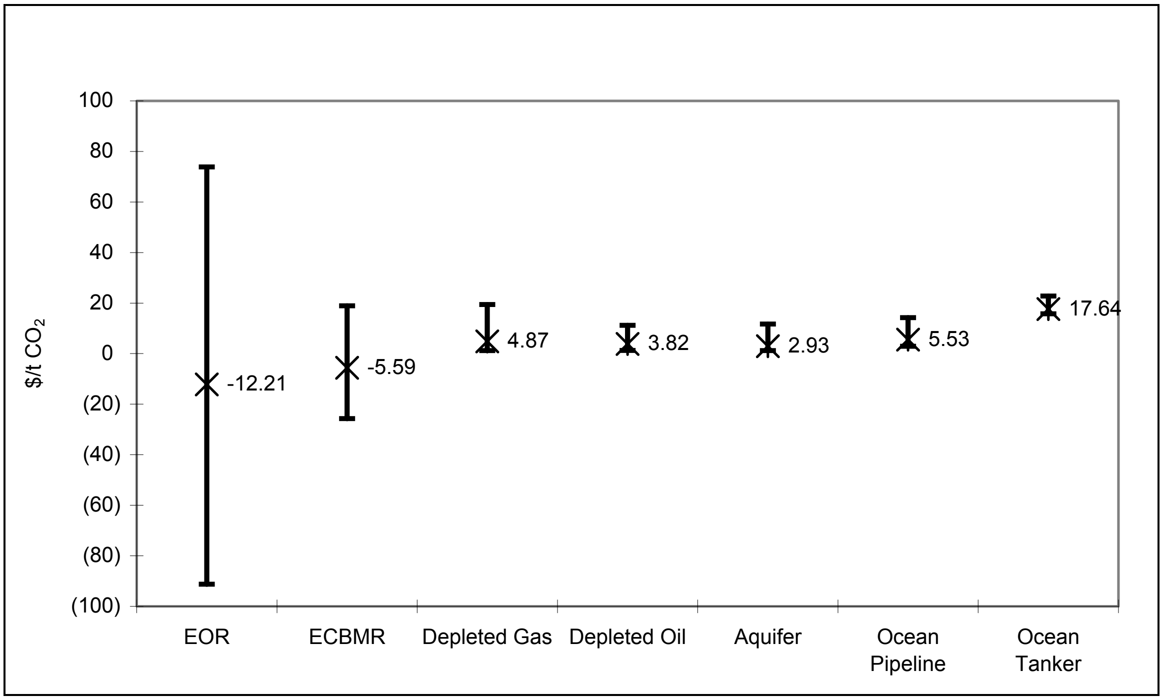

Figure 6. Range of costs for various carbon storage technologies on a greenhouse gas avoided basis.