

Carbon Sequestration

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Abstract

Carbon dioxide (CO₂), a byproduct of hydrocarbon combustion and a natural emission from biomass burning, respiration, or decay, is a major greenhouse gas and contributor to anthropogenic climate change. Carbon sequestration describes the processes by which carbon can be either removed from the atmosphere (as CO₂) and stored, or separated from fuels or flue gases and stored. Carbon sequestration can thus be either technological (usually called carbon capture and storage) or biological (biological carbon sequestration). The viability of carbon sequestration depends on the cost of the process and the policy context that determines the value of sequestered carbon.

INTRODUCTION

The increasingly likelihood of human-caused changes in climate could lead to undesirable impacts on ecosystems, economies, and human health and well-being. These potential impacts have prompted extensive assessment of options to reduce the magnitude and rate of future climate changes. Since climate changes are derived ultimately from increases in the concentrations of greenhouse gases (GHGs) in the atmosphere, such options must target either (a) reductions in the rate of inflow of GHGs to the atmosphere or (b) the removal of GHGs from the atmosphere once they have been emitted. Carbon sequestration refers to techniques from both categories that result in the storage of carbon that would otherwise be in the atmosphere as CO₂.

CO₂ is often targeted among the other GHGs because it constitutes the vast majority of GHG emissions by mass and accounts for three-fifths of the total anthropogenic contribution to climate change. Human emissions of CO₂ come primarily from fossil fuel combustion and cement production (80%), and land-use change (20%) that results in the loss of carbon from biomass or soil.

The rate of inflow of GHGs to the atmosphere can be reduced by a number of complementary options. For CO₂, mitigation options aim to displace carbon emissions by preventing the oxidation of biological or fossil carbon. These options include switching to lower-carbon fossil fuels, renewable energy, or nuclear power; using energy more efficiently; and reducing the rate of deforestation and land-use change. On the other hand, sequestration options that reduce emissions involve the capture and storage of carbon before it is released into the atmosphere.

Keywords: Carbon sequestration; Capture and storage; Carbon sinks; Geologic storage; Climate policy; Emissions trading; Carbon dioxide (CO₂).

Encyclopedia of Energy Engineering DOI:10.1081/E-EEE-120041552
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CO₂ can also be removed directly from the atmosphere. While the idea of a large-scale, economically competitive method of technologically “scrubbing” CO₂ from the atmosphere is enticing, such technology currently does not exist. Policy has therefore focused on the biological process of carbon absorption through photosynthesis, either through expanding forested lands or, perhaps, enhancing photosynthesis in the oceans. This entry describes both the technological and biological approaches to carbon sequestration.

TECHNOLOGICAL SEQUESTRATION: CARBON CAPTURE AND STORAGE

The technological process of sequestering CO₂ requires two steps: first, the CO₂ must be separated from the industrial process that would otherwise emit it into the atmosphere; and second, the CO₂ must be stored in a reservoir that will contain it for a reasonable length of time. This process is therefore often referred to as carbon capture and storage (CCS) to distinguish it from the biological carbon sequestration that is described later.

Sources of Carbon

The best sites for CCS are defined by the efficiency of the capture technique, the cost of transport and sequestration, and the quantity of carbon available. The large capital requirements for CCS also dictate that large, fixed industrial sites provide the best opportunities. Therefore, although fossil-fueled transportation represents about 20% of current global CO₂ emissions, this sector presents no direct options for CCS at this time. The industrial sector, on the other hand, produces approximately 60% of current CO₂ emissions; most of these emissions come from large point sources which are ideal for CCS, such as power

stations, oil refineries, petrochemical and gas reprocessing plants, and steel and cement works.^[1]

Separation and Capture

Carbon capture requires an industrial source of CO₂; different industrial processes create streams with different CO₂ concentrations. The technologies applied to capture the CO₂ will therefore vary according to the specific capture process.^[2–4] Capture techniques can target one of three sources:

- Post-combustion flue gases.
- Pre-combustion capture from gasification from power generation.
- Streams of highly pure CO₂ from various industrial processes.

Post-Combustion Capture

Conventional combustion of fossil fuels in air produces CO₂ streams with concentrations ranging from about 4 to 14% by volume. The low concentration of CO₂ in flue gas means that compressing and storing it would be uneconomical; therefore, the CO₂ needs to be concentrated before storage. Currently, the favored process for this task is chemical absorption, also known as chemical solvent scrubbing. Cooled and filtered flue gas is fed into an absorption vessel with a chemical solvent that absorbs the CO₂. The most common solvent for this process is monoethanolamine (MEA). The CO₂-rich solvent is then passed to another reaction vessel called a stripper column. It is then heated with steam to reverse the process, thus regenerating the solvent and releasing a stream of CO₂ with a purity greater than 90%.

Scrubbing with MEA and other amine solvents imposes large costs in energy consumption in the regeneration process; it requires large amounts of solvents since they degrade rapidly; and it imposes high equipment costs since the solvents are corrosive in the presence of O₂. Thus, until solvents are improved in these areas, flue gas separation by this method will remain relatively costly: just the steam and electric load from a coal power plant can increase coal consumption by 40% per net kWh_e. Estimates of the financial and efficiency costs from current technology vary. Plant efficiency is estimated to drop from over 40% to a range between 24 and 37%.^[2,5,6] For the least efficient systems, carbon would cost up to \$70/t CO₂ and result in an 80% increase in the cost of electricity.^[5] Other studies estimate an increase in the cost of electricity of 25%–75% for natural gas combined cycle and Integrated Gasification Combined Cycle (IGCC), and of 60%–115% for pulverized coal.^[4] A small number of facilities currently practice flue gas separation with chemical absorption, using the captured CO₂ for urea production, foam blowing,

carbonated beverages, and dry ice production. In addition, several developments may improve the efficiency of chemical absorption.

Several other processes have been proposed for flue-gas separation. Adsorption techniques use solids with high surface areas, such as activated carbon and zeolites, to capture CO₂. When the materials become saturated, they can be regenerated (releasing CO₂) by lowering pressure, raising temperature, or applying a low-voltage electric current. A membrane can be used to concentrate CO₂, but since a single pass through a membrane cannot achieve a great change in concentration, this process requires multiple passes or multiple membranes. An alternative use for membranes is to use them to increase the efficiency of the chemical absorption. In this case, a membrane separating the flue gas from the absorption solvent allows a greater surface area for the reaction, thus reducing the size and energy requirements of the absorption and stripper columns. *Cryogenic* techniques separate CO₂ from other gases by condensing or freezing it. This process requires significant energy inputs and the removal of water vapor before freezing.

One of the main limitations to flue-gas separation is the low pressure and concentration of CO₂ in the exhaust. An entirely different approach to post-combustion capture is to dramatically increase the concentration of CO₂ in the stream by burning the fuel in highly enriched oxygen rather than air. This process, called oxyfuel combustion, produces streams of CO₂ with a purity greater than 90%. The resulting flue gas will also contain some H₂O that can be condensed and removed, and the remaining high-purity CO₂ can be compressed for storage. Though significantly simpler on the exhaust side, this approach requires a high concentration of oxygen for the intake air. While this process alone may consume 15% of a plant's electric output, the separated N₂, Ar, and other trace gases also can be sold to offset some of the cost. Oxyfuel systems can be retrofitted onto existing boilers and furnaces.

Pre-Combustion Capture

Another approach involves removing the carbon from fossil fuels before combustion. First, the fuel is decomposed in the absence of oxygen to form a hydrogen-rich fuel called synthesis gas. Currently, this process of gasification is already in use in ammonia production and several commercial power plants fed by coal and petroleum byproducts; these plants can use lower-purity fuels and the energy costs of generating synthesis gas are offset by the higher combustion efficiencies of gas turbines; such plants are called IGCC plants. Natural gas can be transformed directly by reacting it with steam, producing H₂ and CO₂. While the principle of gasification is the same for all carbonaceous fuels, oil and coal require

intermediate steps to purify the synthesis fuel and convert the byproduct CO into CO₂.

Gasification results in synthesis gas that contains 35%–60% CO₂ (by volume) at high pressure (over 20 bar). While current installations feed this resulting mixture into the gas turbines, the CO₂ can also be separated from the gas before combustion. The higher pressure and concentration give a CO₂ partial pressure of up to 50 times greater than in the post-combustion capture of flue gases, which enables another type of separation technique of physical solvent scrubbing. This technique is well known from ammonia production and involves the binding of CO₂ to solvents that release CO₂ in the stripper under lower pressure. Solvents in this category include cold methanol, polyethelene glycol, propylene carbonate, and sulpholane. The resulting separated CO₂ is, however, near atmospheric pressure and requires compression before storage (some CO₂ can be recovered at elevated pressures, which reduces the compression requirement). With current technologies, the total cost of capture for IGCC is estimated to be greater than \$25 per ton of CO₂; plant efficiency is reduced from 43 to 37%, which raises the cost of electricity by over 25%.^[5]

Pre-combustion capture techniques are noteworthy not only for their ability to remove CO₂ from fossil fuels for combustion in turbines, but also because the resulting synthesis gas is primarily H₂. They therefore could be an important element of a hydrogen-mediated energy system that favors the higher efficiency reactions of fuel cells over traditional combustion.^[7]

Industrial CO₂ Capture

Many industrial processes release streams of CO₂ that are currently vented into the atmosphere. These streams, currently viewed as simple waste in an economically viable process, could therefore provide capture opportunities. Depending on the purity of the waste stream, these could be among the most economical options for CCS. In particular, natural gas processing, ethanol and hydrogen production, and cement manufacturing produce highly concentrated streams of CO₂. Not surprisingly, the first large-scale carbon sequestration program was run from a previously vented stream of CO₂ from the Sleipner gas-processing platform off the Norwegian coast.

Storage of Captured CO₂

Relatively small amounts of captured CO₂ might be re-used in other industrial processes such as beverage carbonation, mineral carbonates, or commodity materials such as ethanol or paraffins. Yet most captured CO₂ will not be re-used and must be stored in a reservoir. The two main routes for storing captured CO₂ are to inject it into geologic formations or into the ocean. However, all reservoirs have some rate of leakage and this rate is often

not well known in advance. While the expected length of storage time is important (with targets usually in the 100–1000 year range), we must therefore also be reasonably confident that the reservoir will not leak more quickly than expected, and have appropriate measures to monitor the reservoir over time. Moreover, transporting CO₂ between the point of capture and the point of storage adds to the overall cost of CCS, so the selection of a storage site must account for this distance as well.

Geologic Sequestration

Geologic reservoirs—in the form of depleted oil and gas reservoirs, unmineable coal seams, and saline formations—comprise one of the primary sinks for captured CO₂. Estimates of total storage capacity in geologic reservoirs could be up to 500% of total emissions to 2050 (Fig. 1).

Captured CO₂ can be injected into depleted oil and gas reservoirs, or can be used as a means to enhance oil recovery from reservoirs nearing depletion. Because they held their deposits for millions of years before extraction, these reservoirs are expected to provide reliable storage for CO₂. Storage in depleted reservoirs has been practiced for years for a mixture of petroleum mining waste gases called “acid gas.”

A petroleum reservoir is never emptied of all its oil; rather, extracting additional oil just becomes too costly to justify at market rates. An economically attractive possibility is therefore using captured CO₂ to simultaneously increase the yield from a reservoir as it is pumped into the reservoir for storage. This process is called enhanced oil recovery. Standard oil recovery yields only about 30%–40% of the original petroleum stock. Drilling companies have years of experience with using compressed CO₂, a hydrocarbon solvent, to obtain an additional 10%–15% of the petroleum stock. Thus, captured CO₂ can be used to provide a direct economic

Reservoir Type	Storage Capacity	
	billion tonnes CO ₂	% of <i>E</i>
Coal basins	170	8%
Depleted oil reservoirs	120	6%
Gas basins	700	34%
Saline formations		
Terrestrial	5,600	276%
Off-shore	3,900	192%
Total	10,490	517%

Fig. 1 CO₂ Reservoirs. Carbon dioxide storage capacity estimates. *E* is defined as the total global CO₂ emissions from the years 2000–2050 in IPCC’s business-as-usual scenario IS92A. Capacity estimates such as these are rough guidelines only and actual utilization will depend on carbon economics. Source: Reprinted with permission from Battelle National Laboratory (see Ref. 8).

benefit along with its placement in a reservoir. This benefit can be used to offset capture costs.

Coal deposits that are not economically viable because of their geologic characteristics provide another storage option. CO₂ pumped into these unmineable coal seams will adsorb onto the coal surface. Moreover, since the coal surface prefers to adsorb CO₂ to methane, injecting CO₂ into coal seams will liberate any coal bed methane (CBM) that can then be extracted and sold. This enhanced methane recovery is currently used in U.S. methane production, accounting for about 8% in 2002. Such recovery can be used to offset capture costs. One potential problem with this method is that the coal, as it adsorbs CO₂, tends to swell slightly. This swelling closes pore spaces and thus decreases rock permeability, which restricts both the reservoir for incoming CO₂ and the ability to extract additional CBM.

Saline formations are layers of porous sedimentary rock (e.g., sandstone) saturated with saltwater, and exist both under land and under the ocean. These layers offer potentially large storage capacity representing several hundred years' worth of CO₂ storage. However, experience with such formations is much more limited and thus the uncertainty about their long-term viability remains high. Moreover, unlike EOR or CBM recovery with CO₂, injecting CO₂ into saline formations produces no other commodity or benefit that can offset the cost. On the other hand, their high capacity and relative ubiquity makes them attractive options in some cases. Statoil's Sleipner project, for example, uses a saline aquifer for storage.

Research and experimentation with saline formations is still in early stages. To achieve the largest storage capacities, CO₂ must be injected below 800 m depth, where it will remain in a liquid or supercritical dense phase (supercritical point at 31°C, 71 bar). At these conditions, CO₂ will be buoyant (a density of approximately 600–800 kg/m³) and will tend to move upward. The saline formations must therefore either be capped by a less porous layer or geologic trap to prevent leakage of the CO₂ and eventual decompression.^[9] Over time, the injected CO₂ will dissolve into the brine and this mixture will tend to sink within the aquifer. Also, some saline formations exist in rock that contains Ca-, Mg-, and Fe-containing silicates that can form solid carbonates with the injected CO₂. The resulting storage as rock is highly reliable, though it may also hinder further injection by closing pore spaces. Legal questions may arise when saline formations, which are often geographically extensive, cross national boundaries or onto marine commons.

Ocean Direct Injection

As an alternative to geologic storage, captured CO₂ could be injected directly into the ocean at either intermediate or deep levels. The oceans have a very large potential for storing CO₂, equivalent to that of saline aquifers

(~10³ Gt). While the ocean's surface is close to equilibrium with atmospheric carbon dioxide concentrations, the deep ocean is not because the turnover time of the oceans is much slower (~5000 years) than the observed increases in atmospheric CO₂. Since the ocean will eventually absorb much of the atmospheric perturbation, injecting captured CO₂ into the oceans can therefore be seen as simply bypassing the atmospheric step and avoiding the associated climate consequences. Yet little is known about the process or effects—either ecological or geophysical—of introducing large quantities of CO₂ into oceanic water.

At intermediate depths (between 500 and 3000 m), CO₂ exists as a slightly buoyant liquid. At these depths, a stream of CO₂ could be injected via a pipe affixed either to ship or shore. The CO₂ would form a droplet plume, and these droplets would slowly dissolve into the seawater, disappearing completely before reaching the surface. Depressed pH values are expected to exist for tens of km downcurrent of the injection site, though changing the rate of injection can moderate the degree of perturbation. In addition, pulverized limestone could be added to the injected CO₂ to buffer the acidity.

Below 3000 m, CO₂ becomes denser than seawater and would descend to the seafloor and pool there. Unlike intermediate injection, therefore, this method does not lead to immediate CO₂ dissolution in oceanic water; rather, the CO₂ is expected to dissolve into the ocean at a rate of about 0.1 m/y. Deep injection thus minimizes the rate of leakage to the surface, but could still have severe impacts on bottom-dwelling sea life.

The primary obstacles to oceanic sequestration are not technical but relate rather to this question of environmental impacts.^[10] Oceanic carbon storage might affect marine ecosystems through the direct effects of a lower environmental pH; dissolution of carbonates on fauna with calcareous structures and microflora in calcareous sediments; impurities such as sulfur oxides, nitrogen oxides, and metals in the captured CO₂; smothering effects (deep injection only); and changes in speciation of metals and ammonia due to changes in pH. Few of these possibilities have been studied in sufficient detail to allow an informed risk assessment. In addition, the legality of dumping large quantities of CO₂ into the open ocean remains murky.

Overall Costs of CCS

The costs of CCS can be measured either as a cost per tonne of CO₂, or, for power generation, a change in the cost of electricity (Fig. 2). The total cost depends on the cost of capture, transport, and storage. Capture cost is mainly a function of parasitic energy losses and the capital cost of equipment. Transport cost depends on distance and terrain. Storage costs vary depending on the reservoir but are currently a few dollars per tonne of CO₂. The variety of

Fossil plant type	Cost of CCS
	¢ per kWh
Natural gas combined cycle	1–2
Pulverized coal	2–3
Coal IGCC	2–4

Fig. 2 Additional costs to power generation from CCS. Approximate capture and storage costs for different approaches to power plant sequestration.^[4,5,11,12]

approaches to CCS and the early stages of development make precise estimates of cost difficult, but current technology spans about \$25–\$85/t CO₂.

BIOLOGICAL SEQUESTRATION: ENHANCING NATURAL CARBON SINKS

The previous sections have described processes by which CO₂ could be technologically captured and then stored. Photosynthesis provides an alternate route to capture and store carbon. Enhancing this biological process is therefore an alternative method of achieving lower atmospheric CO₂ concentrations by absorbing it directly from the air.

Terrestrial Carbon Sinks

Carbon sequestration in terrestrial ecosystems involves enhancing the natural sinks for carbon fixed in photosynthesis. This occurs by expanding the extent of ecosystems with a higher steady-state density of carbon per unit of land area. For example, because mature forest ecosystems contain more carbon per hectare than grasslands, expanding forested areas will result in higher terrestrial carbon storage. Another approach is to encourage the additional storage of carbon in agricultural soils. The essential element in any successful sink enhancement program is to ensure that the fixed carbon remains in pools with long lives.

Afforestation involves planting trees on unforested or deforested land.^[13,14] The most likely regions for forest carbon sequestration are Central and South America and Southeast Asia because of relatively high forest growth rates, available land, and inexpensive labor. However, the translation of forestry activities into a policy framework is complex. Monitoring the carbon changes in a forest is difficult over large areas, as it requires not only a survey of the canopy and understory, but also an estimate of the below-ground biomass and soil carbon. Some groups have voiced concern over the potential for disruption of social structures in targeted regions.

Soil carbon sequestration involves increasing soil carbon stocks through changes in agriculture, forestry, and other land use practices. These practices include mulch farming, conservation tillage, agroforestry and diverse cropping, cover crops, and nutrient management

that integrates manure, compost, and improved grazing. Such practices, which offer the lowest-cost carbon sequestration, can have other positive effects such as soil and water conservation, improved soil structure, and enhanced soil fauna diversity. Rates of soil carbon sequestration depend on the soil type and local climate, and can be up to 1000 kg of carbon per hectare per year. Management practices can enhance sequestration for 20–50 years, and sequestration rates taper off toward maturity as the soil carbon pool becomes saturated. Widespread application of recommended management practices could offset 0.4 to 1.2 GtC/y, or 5%–15% of current global emissions.^[15]

If sinks projects are to receive carbon credits under emissions trading schemes like that in the Kyoto Protocol, they must demonstrate that the project sequestered more carbon than a hypothetical baseline or business-as-usual case. They must also ensure that the carbon will remain in place for a reasonable length of time, and guard against simply displacing the baseline activity to a new location.

Ocean Fertilization

Vast regions of the open ocean have very little photosynthetic activity, though sunlight and major nutrients are abundant. In these regions, phytoplankton are often deprived of trace nutrients such as iron. Seeding the ocean surface with iron, therefore, might produce large phytoplankton blooms that absorb CO₂. As the plankton die, they will slowly sink to the bottom of the ocean, acting to transport the fixed carbon to a permanent burial in the seafloor. While some experimental evidence indicates this process may work on a limited scale, little is known about the ecosystem effects and potential size of the reservoir.^[16]

PROSPECTS FOR CARBON SEQUESTRATION

Carbon sequestration techniques—both technological and biological—are elements of a portfolio of options for addressing climate change. Current approaches hold some promise for tapping into the geologic, biologic, and oceanic potential for storing carbon. The costs of some approaches, especially the improved management of agricultural and forest lands, are moderate (Fig. 3). Yet these opportunities are not infinite and additional options

Sequestration Technique	Cost
	\$ per T CO ₂
Carbon capture & storage	26–84
Tree planting & agroforestry	10–210
Soil carbon sequestration	6–24

Fig. 3 Costs of carbon sequestration. Estimates for sequestration costs vary widely.^[4,5,7,11–14] Future costs will depend on rates of technological change.

will be necessary to address rising global emissions. Thus, the higher costs of current technological approaches are likely to drop with increasing deployment and changing market rates for carbon.

Possible developments include advanced CO₂ capture techniques focusing on membranes, ionic (organic salt) liquids, and microporous metal organic frameworks. Several alternative, but still experimental, sequestration approaches have also been suggested. Mineralization could convert CO₂ to stable minerals. This approach seeks, therefore, to hasten what in nature is a slow but exothermic weathering process that operates on common minerals like olivine, forsterite, or serpentines (e.g., through selected sonic frequencies). It is possible that CO₂ could be injected in sub-seafloor carbonates. Chemical looping describes a method for combusting fuels with oxygen delivered by a redox agent instead of by air or purified oxygen; it promises high efficiencies of energy conversion and a highly enriched CO₂ exhaust stream. Research also continues on microbial CO₂ conversion in which strains of microbes might be created to metabolize CO₂ to produce saleable commodities (succinic, malic, and fumaric acids). In addition, the nascent science of monitoring and verifying the storage of CO₂ will be an important element toward improving technical performance and public acceptance of sequestration techniques.

ACKNOWLEDGMENTS

The author thanks the anonymous reviewer for helpful comments on an earlier draft.

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