

An Overview of Carbon Dioxide Sequestration

by Margaret-Gail Medina, Gillian M. Bond, and John Stringer

Increasing public concern about the possible effects that anthropogenic emissions of "greenhouse gases" such as CO₂ may have on global climate has led to a variety of international meetings aimed at limiting these emissions. The UN Framework Convention on Climate Change,¹ for example, calls for capping greenhouse gas concentrations. Although not the most potent of these gases in terms of the greenhouse effect, CO₂ is the one that accounts for much the largest quantity of such anthropogenic emissions, and thus is the focus of most of the debates and research efforts. There is a plethora of possible approaches to carbon management, which is just as well, because the scale of the problem is vast. Annual global emissions, calculated by the Intergovernmental Panel on Climate Control (IPCC),² were around 7.4 gigatonnes* of carbon in 1997, corresponding to 27 gigatonnes of CO₂.

Before discussing methods to reduce these emissions, it is instructive to examine their sources. In general, these can be broken down into buildings (heating, lighting, etc.), transportation, and industry. The proportions of the

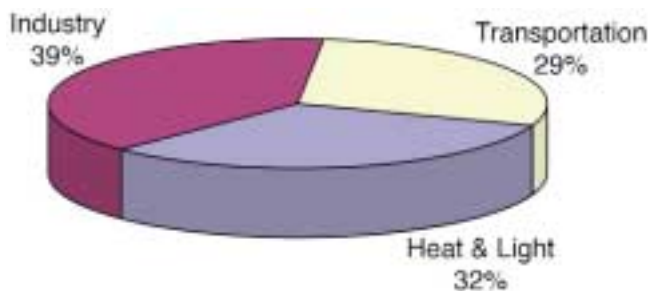


FIG. 1. U.S. CO₂ emissions by sector in 1995. U.S. total = 5.8 Gt C.

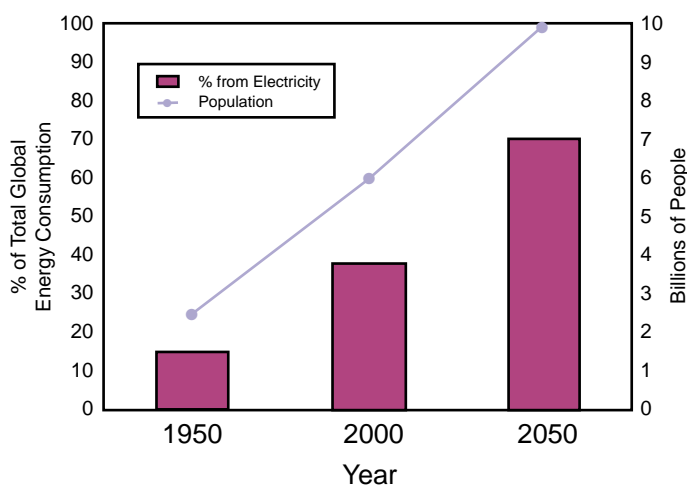


FIG. 2. Trends in global population, and proportion of energy consumption from electricity.

(* Ed. Note: In this article, "tonne" refers to a metric ton)

Table I. Summary of energy options, costs, and benefits.

Energy Source	Examples	Costs	Benefits
Fossil Fuels, Carbon Fuels	Conventional or advanced combustion methods for coal, petroleum, methane, wood, waste, biomass	CO ₂ emissions requiring sequestration, NO _x , SO _x , toxic compounds, altered ecology and climate, loss of biodiversity	Inexpensive, established knowledge base, widespread global deposits of coal, especially in China and India
Non-carbon, Non-combustion	Hydrogen, fuel cells, photo-electric, nuclear fission	Time for research, safety testing, and development	Non-polluting (radioactive waste can be modified or safely stored), advanced materials
Renewables	Solar, geothermal, hydro-electric, tidal, ocean wave, wind	Monitoring and maintenance, altered ecology and biodiversity	Established knowledge base, no emissions

emissions from each of these sectors are fairly similar in the United States, as shown in Fig. 1 (data for 1995).³ Emissions associated with transportation are, of course, predominantly from petroleum, whereas electricity consumption accounts for a substantial part of the emissions from the other sectors.

The most easily addressable type of source of carbon emissions is the generation of electric power, because this represents a relatively small number of very large stationary sources. A representative 300 MW coal-fired power plant, for example, operating at 35% net efficiency (from the coal in, to the electricity delivered to the system busbar) emits ~80 kg of CO₂ per second into the atmosphere. This "typical" plant produces 2.32 tonnes of CO₂ per tonne of coal, or 290 tonnes of CO₂ per hour. The U.S. utility industry as a whole is producing 2.1 billion tonnes of CO₂ per year from coal.³ Furthermore, the percentage of global energy consumption that comes from electricity has been increasing over the last 50 years, and is projected to increase still further over the next 50 years, while world population continues to grow rapidly (Fig. 2). Hence the focus of this paper will be on sequestration in the context of emissions from large fixed sources, such as electricity generation, but first we must address the question, "Why sequestration?"

The Need for Sequestration

The recommendations of scientists to policymakers in the Kyoto Protocol emphasize the immediate need for methods to achieve large-scale decreases in emissions of CO₂ to the atmosphere, adequate to allow the U.S., for example, to decrease emissions by 600 million tonnes of carbon, or 2.2 billion tonnes of CO₂ per year.⁴ Although it is believed that American managed

forests, for example, can sequester 310 million tonnes of carbon annually, terrestrial sequestration alone, (*i.e.* sequestration of CO₂ from the atmosphere by the biosphere), will not be able to absorb enough of the annual global CO₂ emitted (in the U.S. or worldwide) on a suitable time scale. Rather, in order to cap atmospheric CO₂ concentrations, it will be necessary to limit emissions, either by reducing production, or by local capture (at source) and sequestration.

Many avenues are being explored that would enable emissions to be reduced, some of which are reviewed elsewhere in this issue. One obvious group of approaches involves a shift to zero-carbon or low-carbon energy supply and end-use technologies. Major options for energy sources are summarized in Table I. However, coal has been the fuel for a little over half of the electricity generated in the U.S. for many years, and the move away from a fossil-fuel-based energy economy is unlikely to be very rapid. Indeed, in the short to medium term, the generation fleet is likely to be comprised of increasingly fossil-fuel-fired thermal stations. Recently, the generating plant that has been ordered has been comprised of essentially all advanced high-efficiency combustion turbines fired with natural gas. These are relatively cheap to build, burn lower-carbon fuel than coal, and offer higher thermal efficiency (as high as 60%). Natural gas, however, is a significantly more expensive fuel than coal on an energy basis. The technology also exists for the advanced gasification of coal (Integrated Gasification Combined Cycle or IGCC), if natural gas prices become too high, or the availability becomes insufficient. Nevertheless, this still leaves a situation in which considerable amounts of CO₂ will be produced in the course of electricity generation for many years to

come. This is even more apparent when one looks at the global situation.

The U.S. and other developed countries currently account for the lion's share of CO₂ emissions, around 21% coming from the U.S. alone, but this balance will change as energy usage increases in the developing countries. The worldwide average per-capita electricity consumption, in kWh per year, was only 400 in 1950, has risen to 2,100 in 2000, and is predicted to be 6,000 in 2050⁵. [This is based on the following predictions: the developing nations should by then have achieved 3000 kWh per year per person; an aim of 1000 kWh per year per person in the world as a minimum living standard; and an increase in the "electrification of energy" from its present level of 38%, (that is, 38% of all the energy used by people is in the form of electricity), to 70% by 2050.] During the same period of time, the population is expected to increase by perhaps four billion. This would require an increase in global generating capacity from the present figure of 3,000 gigawatts to 10,000 gigawatts. The increased need for food production to support the population means that most agricultural endeavors in the developing countries are likely to remain focused in that direction; consequently large increases in biofuel production are unlikely. Some of the most densely populated developing countries, such as China and India, have large coal reserves, and it is unrealistic to think that these will not be exploited. Putting these factors together, it is clear that neither a more efficient electricity generating plant, nor a move away from carbon-rich fuel, or even from fossil fuels in general, is likely to be sufficient to cap atmospheric CO₂ levels in the next 50 years. Thus there will be a need for local CO₂ capture and sequestration in the interim.

Geological and Marine Sequestration

Most studies on local CO₂ capture and sequestration have been based on the assumption that CO₂ would first have to be concentrated from the exhaust gases from fossil-fuel combustion, and, in general, that it would then have to be transported to a suitable location for disposal. The initial flue-gas composition contains only 10 to 15% CO₂ (Fig. 3).

Technology for concentration and transportation of CO₂ already exists. The techniques most immediately applicable to the case of a fossil-fuel

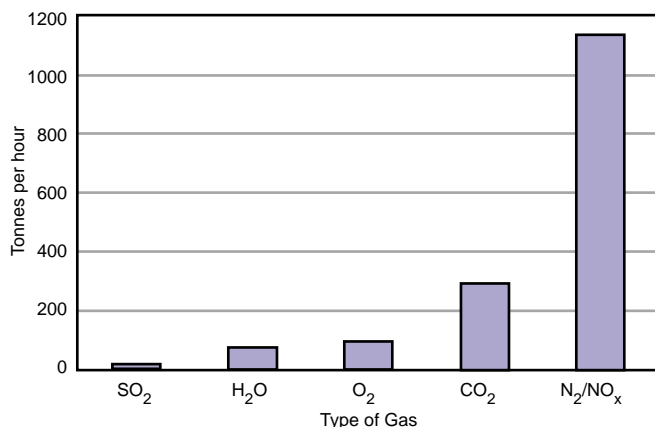


Fig. 3. Representative composition of flue gases for a 300 MW (35% efficiency) coal-burning power plant.

power-plant exhaust would be chemical absorption (typically in alkanolamines such as monoethanolamine), followed by hot steam stripping to produce a concentrated gas stream, and then compression of the gas to form a liquid that can be pumped through pipelines to a sequestration site. There is likely, however, to be a significant economic penalty associated with these processes.

The next issue that arises is where to sequester the CO₂. Various possible sequestration sites have been discussed in the last few years. In general, these sites can be divided into two categories: geological sites and marine sites. Geological and ocean sequestration options are presented, for example, in the Carbon Management Plan.⁶ Some of the advantages and disadvantages are summarized in Table II.

Geological sequestration is seen as the technology that can most rapidly be developed to make significant inroads into the amounts of CO₂ released from fixed sources such as power plants,⁶ and in fact geological sequestration is already being implemented.⁷ The feasibility and expected advantages of geological sequestration have been widely published during recent years.^{5,8} There are, however, aspects of this type of sequestration, as well as marine sequestration, which need further study, particularly in regard to safety.

The concept of sequestering CO₂ gas in depleted oil and gas (DOG) reservoirs is a logical outgrowth of enhanced oil recovery (EOR). This is a petroleum recovery technique, patented in 1952⁹,

that makes use of supercritical CO₂, re-injected into oil wells/reservoirs to help force oil out of crevices where it is otherwise inaccessible. The CO₂ is obtained by chemical absorption in solvents (typically alkanolamines such as monoethanolamine), followed by hot steam stripping to produce a concentrated gas stream, and then compression of the gas to form a liquid. A consortium of oil companies including Statoil, BP, and Shell^{5,7,8} is currently engaged in collaborative research to examine the feasibility of sequestering carbon dioxide in a large underground sandstone formation in the North Sea (the Utsira Formation), as well as conducting pilot studies toward sequestering CO₂ in DOG wells and saline aquifers.

Optimistic claims have been made regarding the large volumes available for geological storage of CO₂. However, there are issues that still need further study, including:

- Unpredictable behavior of CO₂ around the critical point;¹⁰
- Solubility and two-phase behaviors of CO₂;¹¹
- Demonstrated loss of CO₂ to the atmosphere;¹²
- Inability to predict how the gas is moving underground;¹³
- Limited understanding of factors causing injectivity losses;¹⁴ and
- High cost of capture and separation of CO₂ gas from the flue gases, currently assessed at around US \$65.00 per tonne, and rate concerns.¹⁵

Injection of supercritical CO₂ underground requires that the CO₂ will

remain either supercritical, or in solution in water/brine present in the underground formation. These conditions require that reservoirs, aquifers, and other underground formations used for CO₂ storage be at least 800 meters deep. The Utsira formation is 1,000 meters below the seabed, and is believed to be capable of holding a very large volume of CO₂. Nearly one million tonnes of CO₂ were sequestered into this formation last year; it is not, however, a sealed reservoir. None of the geological sequestration locations have been tested for storage integrity under the changing stress conditions that apply for sequestration of very large amounts of CO₂. Flow simulations, for accurate description of permeability, phase equilibria, capillary pressure behavior, and other geophysical factors, are still being developed.^{10,11} Uncertainties in modeling of reaction, transport, and mechanics must be resolved before underground storage systems can be accurately characterized. It should also be borne in mind that, although the amounts of CO₂ currently being injected into formations below the North Sea are substantial, they correspond to only around one third of the output from a single 300 MW coal-fired power plant.

Uncertainties also exist regarding marine sequestration. Carbon dioxide is known to escape from volcanic vents, as in Mammoth Mountain in California, or Lake Nyos, in the Cameroons.¹⁶ In 1986, thousands of people were killed by an involution of this lake. Continuous leakage of under-

Table II. Geological and marine sequestration options: advantages and disadvantages.

CO ₂ Sequestration Method	Advantages	Disadvantages
Geological Deep porous strata, deep saline aquifers, freshwater aquifers, depleted oil and gas wells, deep cool seams or cleats	Large possible volume 810 Gt C (untrapped), in multiple locations worldwide, logical outgrowth of enhanced oil recovery (EOR) techniques	Only 67 Gt C capacity is sealed or trapped, numerous uncertainties regarding mass transport and CO ₂ phase behavior, high cost of gas separation and pressurization, slow rate of separation, 15-20% injection losses, carbonic acid corrosion and pipe leakage, risk of sudden massive (or slow) gas release from repositories
Ocean Very deep ocean, below 1,000 m, shallower regions that favor CO ₂ hydrate formation, surface regions for biological capture processes	Ocean has largest capacity for CO ₂ buffering and storage. Advanced biological methods may promote the conversion of CO ₂ as carbohydrate and protein, or the microbial production of alternate fuels	Cost of gas separation, pressurization, transport and pipeline leakage in highly corrosive setting. Local pH decrease to 4-5 in the immediate vicinity of release (fatal for most marine species), risk of sudden massive release

ground carbon dioxide attained a volume that overcame the pressure of the lake water. It is believed that supercritical carbon dioxide injected to depths below 1,000 meters will be stable because of the low temperatures and high pressures at that depth, but present knowledge of issues such as diffusivity of CO₂ at different depths in the ocean, and deep-sea currents is still very limited. CO₂ gas delivered to depths below 600-800 meters may be dense enough to fall to deeper regions, and remain there unless and until tectonic activity disturbs the equilibrium. At somewhat shallower depths, however, there is the possibility that slow gas leakage into the ocean may at times result in a sudden lowering of water density with tragic consequences. Both methane and CO₂ can leak from areas deep under the seabed. Oil rigs can be sunk by blowouts from these gas pockets. In the North Sea, Witch Ground, 150 meters below the surface, is covered with pockmarks from escaping gas. This area is presently being studied because of a boat from the early 1900s that is sitting upright and entire in an area called Witch's Hole. The scientists studying the wreck believe that gas escaping from the seabed lowered the density of the water, resulting in the sudden sinking of the boat.¹⁷

One laboratory study conducted by the University of Hawaii in conjunction with DOE will track the rate of dispersal of a plume of CO₂ released at depths of up to 600 meters. The introduction of concentrated CO₂ lowers the pH of surrounding waters to between 5 and 6,¹⁸ a range fatal to many organisms, yet this study considers the monitoring of pH as a low priority.¹⁹ Such data must, however, be obtained before large-scale ocean disposal programs are undertaken on the assumption that the large volume of ocean water will buffer large volumes of CO₂ injected over and above the 40,000 gigatonnes of carbon that the ocean already holds. Ocean water contains several poorly understood buffering systems, which are hard to reproduce in laboratory experiments.

Alternative Approaches to Geological Sequestration

Sequestration of CO₂ in the form of a stable, environmentally friendly solid would have obvious appeal for safe long-term storage. Indeed, carbonate minerals, such as calcite, aragonite, dolomite, and dolomitic limestone, constitute the earth's largest CO₂ reservoir, estimated to contain an amount of carbon equivalent

to 150,000 x 10¹² tonnes of CO₂.²⁰ Thus the geological record demonstrates that large amounts of CO₂ can be stored indefinitely in carbonate form. Two types of geological processes have led to the formation of much of these carbonate minerals, each of which can be viewed as a model for the sequestration of anthropogenic CO₂:

- ▶ Generation of carbonates by the silicate-to-carbonate exchange, in which the byproduct is silica. Work is ongoing at Los Alamos National Laboratory²¹ to develop an analogous process, based on carbonation of serpentinites and peridotites, which could be used on an industrial scale and timeframe. One potential advantage of this approach is that the carbonation reaction is exothermic.
- ▶ Generation of calcium carbonate by various types of marine animals, forming, for example, the very extensive oolitic limestone beds. Work is ongoing at New Mexico Tech²² to develop an analogous (biomimetic) process, in which a biological catalyst, the enzyme carbonic anhydrase, is used to accelerate an aqueous processing route to carbonate formation. Potential advantages of this biomimetic approach include the possibility of an on-site scrubber that would provide a plant-by-plant solution to CO₂ sequestration, as well as avoiding the need for concentration and transportation of CO₂.

There is another possible variation on the theme of geological sequestration, which also has a biomimetic component. The vast majority of methane in the earth's crust appears to be biogenic in origin.²³ In some gas fields, the methane is generated exclusively by the action of methanogen bacteria, via a CO₂-reduction pathway. It has been proposed that a "closed-loop" fossil-fuel carbon cycle could be developed, in which an enhanced microbial consortium is used to convert CO₂ to methane at a commercially useful rate, either in a geologic setting (following injection of CO₂ into a DOG well, saline aquifer, etc.), or above ground in rapid-contact reactors.²³

Conclusions

A range of carbon management strategies will have to be implemented if meaningful reductions in CO₂ emissions are to be achieved in the coming decades. These include improvements in the efficiency of electricity genera-

tion and usage, accelerated decarbonization of fuels, and a shift to an energy economy that is not based on fossil-fuel combustion. It is clear, however, that there will also be a need, in the interim (the next 20-40 years), for capture and sequestration of CO₂ emitted from, for example, the coal-fired power plants that currently generate more than half the world's electricity. Several possible approaches to sequestration have been discussed in this article. All of them still have issues that need to be addressed, whether in relation to development of the basic technology, or in relation to questions of safety, efficiency, and/or cost, and thus continuing research on sequestration is essential. ■

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