

Sustaining Fossil Fuel Use in a Carbon-Constrained World by Rapid Commercialization of Carbon Capture and Sequestration

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Introduction

Briefly stated, carbon capture and sequestration (CCS) will allow us to sustain many of the benefits of access to hydrocarbons even in a carbon constrained world. Even where the CO₂ generated by burning hydrocarbon cannot be captured easily (as in the case of oil use for transportation), sequestration of CO₂ from other sources (e.g., coal fired power stations) can help create, to some degree, the "headroom" needed to allow for the volumes of CO₂ which escape capture. Because of the likely continuing competitive (direct) cost of hydrocarbons, and in light of the huge investment already made in infrastructure to deliver them, the combination of fossil fuel use with CCS is likely to be emphasized as a strong complement to strategies involving alternative, nonhydrocarbon sources of energy supply. Moreover, concerns about the security of supply of transportation fuels are likely to drive moves toward less conventional hydrocarbon sources (coal-to-liquids, unconventional oil and gas, etc.). However, the exploitation of heavy oil, tar sands, oil shales, and liquids derived from coal for transportation fuel comes with a significantly heavier burden of CO₂ than is associated with conventional oil and gas. CCS has the potential to mitigate some of this extra CO₂ burden, provided it is implemented broadly over the coming decades. Widespread use could continue beyond the end of the century.

Here we lay out arguments for identifying CO₂ as a key determinant of modern climate change and outline some of the technology developments needed to address CO₂ emissions without unreasonably impacting the world's future energy needs.

Paleoclimate

The Vostok ice core¹ provides a continuous record of Antarctic climate and greenhouse gases over the last 420,000 years, a temporal record which has recently been extended to 800,000 years by the Antarctica Dome C core.² The relative abundances of Hydrogen and Oxygen isotopes trapped in these cores give a good indication of local temperatures over this period, and air bubbles trapped in the ice yield a detailed record of atmospheric composition over time, including the levels of the greenhouse gases carbon dioxide and methane.

The last four ice ages, each about 100,000 years long, are evident in the Vostok temperature record. The transition between glacial and interglacial conditions is driven by a distinctly nonlinear coupling of a variety of mechanisms: Variation in the earth's orbital parameters leads to a modulation of the geographical distribution of the flux of solar energy received by the earth. This is revealed in the graph of the mid-June insolation at 65 deg North (in Watts per square meter (W/m²)) appended to the Vostok data shown in Figure 1. At the end of an ice age, this variation in insolation causes an enhanced seasonal warming at the poles (with the northern polar region possibly playing the key role),³ which is amplified by at least two mechanisms which increase the total energy flux absorbed by the earth (so called "radiative forcing"). These mechanisms include a (global) warming associated with

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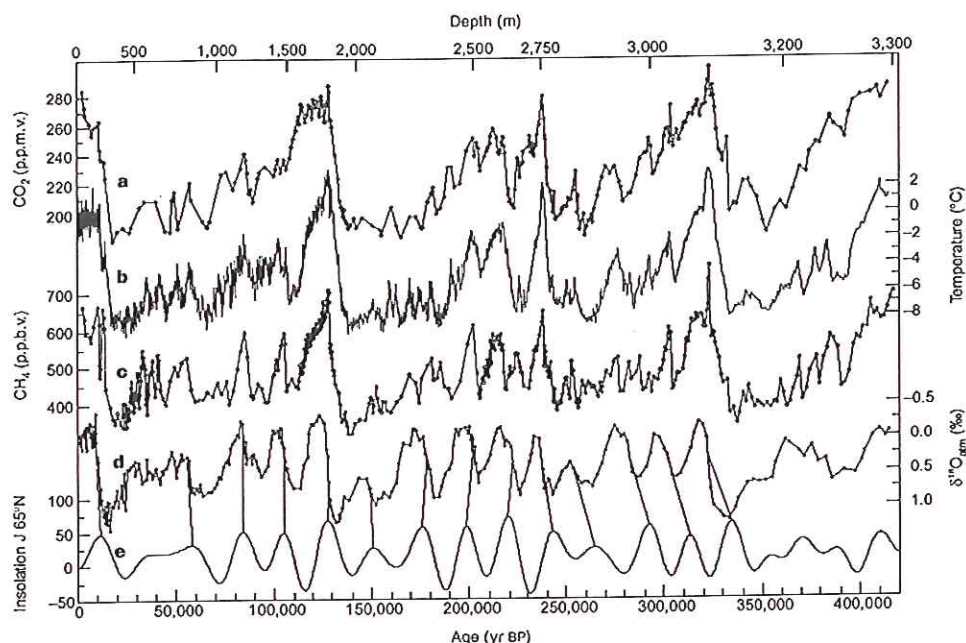


Figure 1. Vostok ice core data showing CO₂ concentrations (a), inferred temperature (b), methane concentrations (c), and variation in the atmospheric O₂ isotopic composition (d), appended is the insolation curve (e) with inferred correlation points tying the timescale calculated for the ice data to the independently determined timescale for the insolation signal: the inferred temperature is a function of the isotopic composition of the ice and is described in detail in Ref. [1].

an increase in atmospheric carbon dioxide (and to a lesser extent methane), and a reduction in the solar flux reflected back from the earth's surface as polar ice melts.¹ A substantial fraction of the radiative forcing required to produce the transitions from glacial maxima to the warmer interglacials stems from the rise in CO₂ levels. Without the extra forcing terms, and in particular without the 40% rise in CO₂ levels, the earth would not emerge from the ice ages. The mechanisms responsible for the rise in CO₂, which is highly correlated to temperature, are not fully understood,⁴ but are likely to involve variations in biological activity, decreased stratification⁵ of the ocean in the warmer conditions (influencing the interchange of CO₂ between the atmosphere and the oceans), and other physical effects.

Modern Climate Change

The earth emerged from the last glacial period into the current interglacial, the Holocene, with atmospheric CO₂ levels of about 280 ppmv (as had prevailed during the previous interglacials). Subsequently, the CO₂ level began to rise only in the two centuries since the industrial revolution, and in the last fifty years in particular. The current level of 380 ppmv exceeds those of any time in the last 2 million years (and probably the last 25 million years).

The recent rise in CO₂ levels has been accompanied by a rise in global temperature, as well as other associated changes:⁶

- Marine air temperatures have increased by 0.4–0.7 deg C since late 19th century
- Sea surface temperatures have increased by 0.4–0.8 deg C since late 19th century

- Land nighttime temperatures have been increasing at twice the rate of daytime temperatures since 1950

- Northern hemisphere spring snow cover has decreased by 10% over the last 20 years (compared to the mean level for the period 1966–1986)

- There has been widespread retreat of mountain glaciers during the 20th century

- Both the maximum extent and minimum extent of arctic sea ice have fallen, indicative of warmer conditions in the arctic. Since the 1950s there has been a 10%–15% reduction in the springtime extent of arctic sea ice, and a possible reduction of 40% in the late summer ice thickness.

Of these, the reduction in arctic sea ice, shown on the front cover of this journal, is possibly the most alarming, as it raises the prospect of an associated melting of the Greenland ice sheet itself.⁷

Carbon Emissions and the Buildup of Atmospheric CO₂

As shown in Figure 2,⁸ human emissions of carbon dioxide started to escalate with the industrial revolution and currently humanity generates about 8 billion tons of carbon (almost 30 billion tons of CO₂) each year. The natural annual net emission of CO₂, largely from volcanoes, averages about 1% of this figure.⁹ CO₂ emissions derived from the burning of wood and fossil fuels since the start of the industrial revolution fully account for the more than 30% increase in atmospheric levels of CO₂ over this period. Indeed, had half of these emissions not found their way to dissolution in the world's oceans, atmospheric levels of CO₂ would

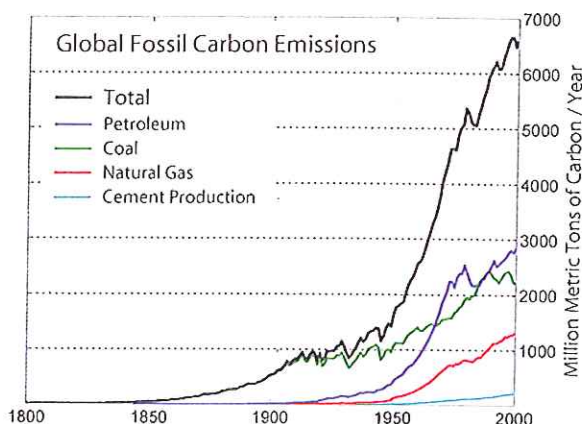


Figure 2. Growth of the major components of anthropogenic CO₂ emissions since 1800.⁸

already be approaching double the preindustrial level of 280 ppmv.

Oil currently accounts for 39% of fossil-fuel related CO₂ emissions and gas for 20%, while coal accounts for the remaining 41%.¹⁰ All in all, hydrocarbons presently provide about 85% of the world's primary energy supply.

Mitigation Strategy: Avoiding a Manmade Eemian

If we continue the current escalation of CO₂ emissions we are likely to incur mean global temperature rises well in excess of 2°C (possibly as high as 5°C)⁶ by the end of this century, and atmospheric CO₂ concentrations destined to rise above 1,000 ppmv in the following century. We will have exceeded the temperature conditions of the last interglacial period (the Eemian), which was just a few degrees warmer than the current interglacial (the Holocene). The consequence of these higher temperatures for the Eemian was that sea levels, augmented by a greater degree of melting of probably both the Greenland ice sheet and the West Antarctic ice sheet, were 4–6 m higher than they are today.¹¹ Had our civilized societies emerged during the Eemian rather than in the Holocene we would have had very different coastlines, and we would have chosen very different locations for many of our cities and for much of our farmland.

It now appears that an inadvertent consequence of our civilizations' technology choices may be the development of a world resembling the Eemian after all, but unfortunately after we have established our existing human geography. Within a few centuries, the melting and destabilization of substantial parts of the Greenland ice sheet along with parts of the Western Antarctic ice sheet would inevitably lead to sea levels comparable to those of the Eemian.

By How Much Do We Need to Curb CO₂ Emissions?

The IEA predictions¹⁰ for energy demand and the concomitant dependence on fossil fuels will, if realized, lead to annual global CO₂ emissions of about 60 billion tons by 2055—about twice today's levels. If, on the other hand, we can limit

annual emissions during the next fifty years to less than about 25 billion tons, and subsequently reduce them to about 10 billion tons annually, then the total concentration of CO₂ in the atmosphere will asymptote to about 550 ppmv and Eemian conditions could be avoided.^{7,12,13} Pacala and Socolow¹² argue that no single strategy could do the whole job, but that parallel campaigns that scaleup strategies already commercialized somewhere in the world could suffice. The key elements of such a strategy would be:

- Carbon capture and sequestration;
- Energy efficiency and demand reduction;
- Switching from coal to natural gas;
- Shift to alternative energy sources;
 - Wind;
 - Photovoltaic;
 - Nuclear;
 - Biomass;
- Forest management;
- Agricultural soils management.

Of these, carbon capture and sequestration (CCS) will play a critical role so long as we continue to depend on fossil fuels. CCS is best matched to centralized power generation. Where fossil fuels are widely distributed and used at small-scale—in ground and air transportation, and building space heating—CCS is not viable, and must be augmented with improvements in efficiency, electrification (plug-in hybrid vehicles, heat pumps), demand reduction, and the development of alternative energy sources.¹⁴

Geological Sequestration of Carbon Dioxide

Two regions of the earth have been proposed for sequestering CO₂: the oceans and porous geological structures beneath the earth's surface.¹⁵ Sequestration of CO₂ in the oceans seems unlikely; the continuing acidification of the ocean,¹⁶ caused by the dissolution of anthropogenic CO₂, already raises serious alarms about human impacts. More tractable, however, is geological sequestration, where supercritical CO₂ is pumped into spent oil and gas reservoirs or deep saline formations. CO₂ sequestration for a few thousand years, with no large sudden releases along the way, is sufficient for CCS to play a major role in climate change mitigation.

Viability of Carbon Capture and Geological Sequestration

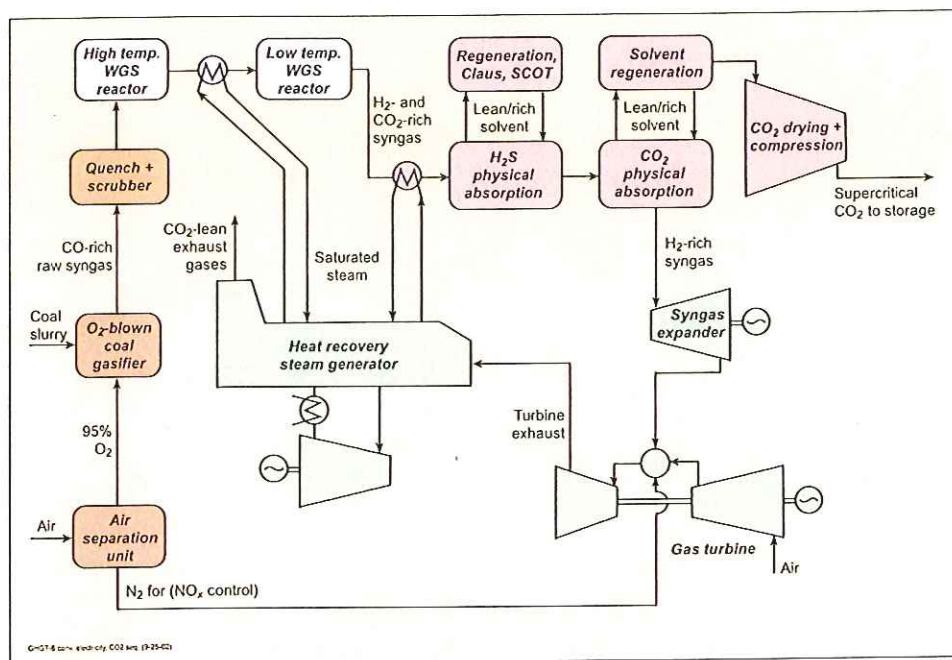
CO₂ capture

Currently there are three main approaches to capturing the CO₂ generated by a coal-fired electricity plant.

In traditional pulverized coal plants the coal is burnt in an air stream, leaving the postcombustion flue gasses, with a CO₂ con-

⁸We may consider more challenging technology, such as direct removal of atmospheric CO₂,^{17–21} and geo-engineering to modify the earth's albedo.²²

¹¹There are also suggestions to implement mineral sequestration,²³ although such proposals are at a relatively early stage, and the practicality of implementation has not yet been fully explored.



centration of approximately 15% (by volume). Solvents, or potentially membrane technologies, can be used to extract this relatively dilute CO₂ component. For example, CO₂ can be captured by dissolution of the flue gases in a monoethanolamine (MEA) solvent at a temperature of 38°C, followed by heating the MEA solvent to 150°C, leading to its re-release as a concentrated CO₂ stream. This relatively pure CO₂, once compressed, would be ready for transfer to a suitable sequestration site. At present, about 30% of the total heat energy generated by the plant is required to drive the high-temperature desolution of the CO₂ from the MEA solvent,¹⁶ and capture accounts for more than 80% of the entire cost for capture and sequestration. Alternative approaches, including the “chilled ammonia” process (where absorption is carried out in a slurry of ammonium carbonate and bicarbonate), and high-temperature sorbent paths using, for example, limestone, are currently being explored.

The "oxyfuel" process, burning coal in an atmosphere enriched in oxygen, eliminates most of the nitrogen, and leads to a much more concentrated CO₂ stream at the outlet. Conventional cryogenic oxygen separation requires about 28% of the generated energy.²⁴

Precombustion separation, as seen in Figure 3,²⁵ begins with coal gasification at high-temperature with steam and oxygen. The resulting syngas, mainly carbon monoxide and hydrogen, also contains H₂S, NH₃ and Hg. A further shift reaction with steam will produce a stream of H₂ and CO₂ (15–40%) at pressures in the range 1.5–4 MPa. The CO₂ can be separated at high-pressure using for example physical absorption or a membrane, leaving a highly concentrated hydrogen stream. The hydrogen, burnt in air, drives a turbine, and its hot exhaust drives a second turbine. Such integrated gasification combined cycle (IGCC) processes may limit the incremental retail electricity cost for the CO₂ capture to about 20%.²⁶

Capture costs may be lowered by new membrane technology with high-permeability, and good chemical selectivity, along

with good performance at high-temperature. Other technologies, such as chemical looping,²⁴ where, for example, iron oxide partially oxidizes coal, and the metallic iron subsequently reacts with steam to release hydrogen, may also play a role.

CO₂ can also be made available for capture at large scale and high concentration elsewhere than at power plants. Where hydrogen is produced from natural gas, petroleum, or coal for direct use in refineries or as a precursor to ammonia production at fertilizer plants, there is frequently an exhaust stream of nearly pure CO₂. Where natural gas emerging at the well-head contains too much CO₂ to meet regulatory requirements for grid injection, the CO₂ is routinely removed, along with other combustible and noncombustible gases. These streams of CO₂ are among the lowest-cost CO₂ capture opportunities.

It may prove advantageous to capture and sequester other pollutants along with CO₂, thereby reducing the above-ground costs of pollution control. New approaches to sulfur management are particularly intriguing. CO₂ capture technology may capture SO₂ in the flue in the case of postcombustion capture, or H₂S in the case of precombustion capture. However, there may be countervailing complications related to co-storage, notably greater stringency in the rules for handling the gas mixtures, relative to pure CO₂.

Geological storage of CO₂

Once captured, the concentrated CO₂ stream must be transported to a suitable storage site. CO₂ transport is already a mature technology and costs are relatively low. CO₂ is currently transported in pipes as a supercritical fluid (above 8MPa), and as a low-temperature liquid in ships or by road or rail. In the US more than 40Mt CO₂ a year is distributed through a network of over 2,500km of pipes.²⁷

The degree of CCS required in a carbon constrained world is, however, not inconsiderable. By the year 2055, based on

current possible scenarios for climate change,^{12,28} it will be necessary to mitigate at least eight billion tons of carbon per year, of which four or five might come from substitutions for conventional coal power. Geological sequestering of one billion tons of carbon per year would entail pumping about 90 million barrels (bbls) per day of supercritical CO₂ into geological formations. This amounts to about a quarter of the volume of water currently pumped worldwide for secondary oil recovery. At the local level, sequestering CO₂ from a 1GW coal fired power station²⁶ would require pumping around 150,000 bbls/day of supercritical CO₂ into a suitable formation.*

The technologies and expertise needed to sequester such volumes already reside within the oil and gas industry. Several demonstrations of CO₂ sequestration are currently underway, and include the "In Salah" saline formation project in Algeria²⁹ and the "Sleipner" project offshore Norway. In the Sleipner project, Statoil has successfully pumped over 1 million tons of CO₂ per year for the last 10 years into the deep saline Utsira formation, which lies about 1,000m beneath the sea bed, capped by a low-permeability shale layer.

Available Pore Space. It appears likely that there is ample pore space below ground to store the necessary quantities of CO₂.²⁷ Spent oil and gas reservoirs provide space for hundreds of billions of tons of CO₂, while deep saline aquifers provide room for an order of magnitude more than this. Note that the amount of CO₂ storage space below ground is not a fixed quantity. Rather, pore space for storage in sedimentary formations is like any other fuel or mineral reserve, whose quantity changes with time, increasing as science and technology improve and rising as well with the price people are willing to pay.

Physical and Chemical Behavior of CO₂ in the Formation. The secure storage of CO₂ in geological formations depends on a number of physical and chemical mechanisms. At a depth between 600m and 1,000m temperature and pressure combine to produce an environment where CO₂ is a supercritical fluid with a specific density between about 0.6 and 0.8.³⁰ Buoyant in the formation waters, it rises until it encounters a sealing formation whose quality as a barrier depends on an absence of fractures or discontinuities. Determining seal characteristics is a critical part of storage site appraisal. In the case of exhausted oil and gas reservoirs these features will generally be known sufficiently well; this is not the case, however, for the deep saline formations which ultimately may provide most of the storage space. Surveying and appraising such storage formations represents a substantial task.

Once in the formation, some of the injected supercritical CO₂ will be trapped along its migration path by capillary forces. This "residual trapping" may account for between 5 and 30% of the injected volumes.³⁰ More slowly, over several thousand years, the CO₂ will dissolve in the native brines. The CO₂ laden brine is denser than the surrounding fluids, and it will consequently sink through the formation. The dissolved CO₂ renders the brines acidic, allowing them to dissolve carbonate and aluminosilicate minerals, leading, in turn, to "mineralization"—the storage of CO₂ via precipitation of solid carbonates—with a characteristic timescale of hundreds to thou-

sands of years. Detailed geophysical and geochemical modeling of these storage mechanisms is key to predicting the long-term fate of geologically sequestered CO₂.

Storing CO₂ in coal. CO₂ can be absorbed onto the surfaces of microporous structures, and, in particular, CO₂ will displace absorbed methane from coal. However, although the methane driven off has economic value, it represents a significantly smaller energy resource than the coal itself, and the use of coal beds for CO₂ storage makes sense only if the coal is destined to be left permanently in place. Furthermore the process is attractive only in coal beds of unusually high-permeability. Nonetheless, storage of CO₂ in suitable coal beds may contribute to CCS to some degree.

Leakage. CO₂ can breach a seal through a fracture or fault. The CO₂ injection process itself may initiate fractures or enhance the permeability of faults, and dissolved CO₂ may migrate through natural flow. The rate of its further migration will be controlled by permeability to CO₂ in the overlying formations, and CO₂ may ultimately escape to the atmosphere or to a body of water. Existing monitoring techniques lend themselves to observing many of these processes. In particular, repeated seismic surveys can be used to follow the migration of injected CO₂, as lower density CO₂ displaces higher density brine, thereby modifying the local acoustic properties of the formation.³¹ Other techniques, such as electric logging and gravity surveying, already used in the oil and gas industry, will also find application.

Largely unexplored, but of significant interest, is the potential for injecting CO₂ in combination with suitable treatment fluids, which enhance or secure sealing of the storage volume. Treatments which modify the permeability of formations to supercritical CO₂, or which accelerate the mineralization or otherwise immobilize CO₂, would have an enormous impact on the potential of carbon sequestration.

Leakage Through Old Wells. When exhausted oil and gas reservoirs are targeted for CO₂ storage, the long-term integrity of the suite of wells previously drilled to exploit the resource becomes a determinant of the long-term security of storage, since these wells inevitably penetrate the sealing structures which originally trapped the oil or gas, and which will now be required to trap the CO₂.³² The cements used to provide a gas tight seal between the steel lining of the wells and the formation are a particular concern, because they are prone to attack by formation waters rendered acidic by the introduction of CO₂. The overall leakage potential and remediation requirements are poorly known and represent a significant chemistry challenge.

Particular Cases of Petroleum Coke and Biomass

The issues and choices presented by capture from a coal power plant are very similar for other solid fuels, notably petroleum coke and biomass. Petroleum coke (petcoke), the "bottom of the barrel" residual left by the world's refineries, is essentially identical to a good quality coal, as far as capture is concerned. Its cost at the refinery is very low, but in coun-

*We assume 9 bbl = 1 ton (specific gravity of 0.7), and 6 MtCO₂/yr emissions from a 1 GW coal plant.

tries with strict air pollution rules it cannot be burned for power. However, gasification of petcoke, along with carbon capture, enables the removal of pollutants at high-pressure. Consequently a 6% sulfur petcoke (a typical figure) can be readily accommodated. At BP's 260,000 bbl/day Carson refinery near Long Beach, California, there are plans to gasify 4,500 t/day of petroleum coke, generating 510 MW while 4 Mt CO₂/yr are compressed and sent offsite for sequestration (in this case, twinned with enhanced oil recovery).^{33,34}

Likewise, a biomass power plant will gasify and chemically "shift" the feedstock to a mixture of CO₂ and hydrogen, separate the two gases, capture and export the CO₂ for storage, and make power from the hydrogen. In this case, however, the power plant has scrubbed the atmosphere of CO₂, because the carbon in the biomass was "fixed" earlier by photosynthesis.³⁵

Enhanced Oil Recovery using CO₂

CO₂ is already pumped into oil reservoirs for enhanced oil recovery (EOR), because it is very effective at mobilizing oil, particularly late in the life of an oil reservoir. Currently most of the CO₂ used for EOR comes from natural sources, and existing EOR practices are not implemented with a view to storing the CO₂. However, it is possible to modify the CO₂-EOR to emphasize such CO₂ storage, while at the same time improving oil recovery. Although EOR-associated storage could accommodate only a small fraction of the volume of CO₂ the world will eventually store if CCS becomes a major factor in carbon mitigation, it could provide a bridge to the technologies required for routine sequestration, driven by the commercial incentives to improve recovery of the oil from older reservoirs. Moreover, in a world where CO₂ is much more readily and cheaply available, there will be an incentive to use CO₂ earlier in the oil recovery stage to better exploit dwindling resources.

Chemistry Challenges for Carbon Capture and Sequestration

We have outlined here a number of important technical challenges along the path to effective carbon capture and sequestration. These include:

- Developing innovative approaches to CO₂ capture, which significantly reduce the current costs of separation. Capture using current technologies would account for well over half the total cost of CCS, and so capture represents a huge opportunity for technological improvement. Possible technologies will include physical and chemical absorption, high-temperature sorbents, membranes and cryogenic separation. Improved capture techniques will find a place not only in power plants, but also in synfuel production and other industrial settings.
- Understanding the long-term geochemistry of CO₂ in subsurface formations. In particular we need to be able to predict the migration of CO₂ plumes, their physical and chemical interaction with sealing rocks, and their tendency to form solid minerals leading to almost indefinite sequestration of CO₂.
- Modifying the chemical and physical behavior of CO₂ in geological formations to enhance secure storage.
- Identifying and developing suitable materials for secure conduits to the CO₂ storing formations and developing media-

tion techniques to treat the abandoned wells which perforate the seals of storage formations.

- Establishing the necessary suite of measurement and appraisal techniques to reliably and routinely characterize the target formations for CO₂ sequestration in terms of capacity, injectivity and security (including geochemical evolution). Monitoring technology will need to include chemical sensors and tracers tailored to measure CO₂ migration and leakage.

Moreover, for CCS to become a viable, routine climate mitigation strategy, a number of key societal initiatives are necessary.¹⁴

- Launching CCS through several full-scale projects that integrate capture of CO₂ at coal-fired electricity generating stations with subsequent compression and sequestration of the CO₂ into an appropriate formation, for a variety of coal types, capture strategies, and types of storage formations.

- Identifying, through national surveys, suitable formations (both spent oil and gas reservoirs and deep saline formations), where CO₂ can be securely stored.

- Establishing an infrastructure of pipelines for CO₂ transport which is sufficient to the task of effectively dealing with the large volumes of CO₂ involved.

- Establishing a clear regulatory framework which encourages and facilitates CCS.

- Establishing an effective, predictable cost for carbon emissions to create incentives to curbing CO₂ emissions.

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