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# Carbon Dioxide Reuse and Sequestration: The State of the Art Today

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## Abstract

Atmospheric concentrations of CO<sub>2</sub> and other greenhouse gases (GHGs) are growing steadily. GHG levels seem likely to grow more quickly in the future as developed countries continue to use large amounts of energy, while developing countries become wealthy enough to afford energy-intensive automobiles, refrigerators, and other appliances (as well as live and work in larger, more comfortable structures). To keep GHGs at manageable levels, large decreases in CO<sub>2</sub> emissions will be required. Yet analysts understand the difficulty of developing enough zero- and low-carbon-emission technologies to meet the goal of safe GHG stabilization.

Carbon sequestration technologies can help bridge this gap. These technologies are only beginning to be developed, but their promise is already evident. In Europe, CO<sub>2</sub> has been continuously and safely pumped into a below-sea limestone structure for over three years, where it remains. In New Mexico, CO<sub>2</sub> is being used to drive out natural gas from within unminable coal seams 1,000 meters below the surface, and again, continuously injected CO<sub>2</sub> has stayed sequestered for over three years, even though the project was designed for natural gas production, not CO<sub>2</sub> sequestration. These and other beginnings suggest that much CO<sub>2</sub> could be reused or sequestered over time. However, substantial R&D will be required so that CO<sub>2</sub> can be captured inexpensively, and then reused or safely sequestered economically. Advanced concepts likely hold great promise as well.

## Introduction

Atmospheric concentrations of greenhouse gases (GHGs) such as carbon dioxide (CO<sub>2</sub>) are growing steadily. The more such concentrations grow, the greater the potential for serious problems that could disturb the working of the planet's natural systems. But controlling the growth of GHGs, and sharply reducing worldwide emissions, will be difficult. Developed countries are responsible for the highest rates of GHG emissions per capita, with the U.S. the world's largest emitter of GHGs. Less-developed countries aspire to what are now mostly western amenities; as such countries become wealthier, their citizens purchase and use cars, refrigerators, larger and tighter homes, and appliances. As office buildings and factories are built, energy and electricity use rises. China and India account for 1/3 of the world's population between them and are among the countries with the fastest-growing economies. Clearly, the potential for further GHG accumulation is great.

To deal with GHGs, we in the energy field will have to rapidly advance the technology for low-carbon- and no-carbon-emitting sources of electricity, including renewables, wind, and highly efficient fuel cells and combined cycle equipment. We will also need to use energy increasingly

more efficiently as time goes on. But these actions in themselves will not likely be adequate to bring atmospheric concentrations of GHGs low enough to stabilize them at a safe level, the aim of the 1992 Rio de Janeiro treaty on GHGs.

Not many people know about the promise of reuse and sequestration (storage) of the principal GHG, CO<sub>2</sub>. However, informative articles like that in the February 2000 *Scientific American*, 'Capturing Greenhouse Gases', are helpful in spreading the word. Along with advancing technology and using energy more efficiently to reduce emissions, CO<sub>2</sub> sequestration and reuse are likely to be a major part of a multifaceted solution to the GHG problem.

Throughout the world, CO<sub>2</sub> sequestration efforts have quietly begun. Few may know that CO<sub>2</sub> is currently being sequestered in Europe, in a briny sandstone formation 800 meters under the seabed in the North Sea; that this process has been ongoing for over three years; or that such formations in Europe hold the promise to sequester much of Europe's incremental CO<sub>2</sub> emissions from stationary sources for the next several decades. Few people know that CO<sub>2</sub> is currently being used as a sort of solvent to drive out marketable methane from unminable coal seams 1,000 meters deep in New Mexico, and that the CO<sub>2</sub> has been staying put for over three years, sequestered within coal molecules (as predicted by geochemists).

Both of these projects are 'first of a kind'. Much more science needs to be done to understand how they might be replicated in somewhat different formations elsewhere. Much more R&D is also needed to explore many other issues of CO<sub>2</sub> reuse and sequestration as well. But we are off to a promising start.

Below, you will read more about some of the proposed or ongoing work to answer the many questions surrounding the reuse and sequestering of CO<sub>2</sub>. Indeed, sequestration of CO<sub>2</sub> is in its infancy, and proposals to reuse (recycle) CO<sub>2</sub> are only now beginning to emerge. At present, the state of the art is nascent, but already it includes real-world projects with early breakthrough technologies and new concepts to reduce costs, new science to understand environmental impacts of new proposals, and new insights that might enable us to recycle CO<sub>2</sub> as usable fuels, chemicals, or materials.

The remainder of this overview will discuss five subject areas for CO<sub>2</sub> sequestration or reuse. These are:

- (1) Geologic Sequestration
- (2) Separation and Capture of CO<sub>2</sub>
- (3) Advanced Concepts for CO<sub>2</sub> Reuse or Sequestration
- (4) Sequestration in Terrestrial Ecosystems
- (5) Ocean CO<sub>2</sub> Sequestration

Substantial detail on the state of the art for all of these subject areas is available in the report, *Carbon Sequestration: State of the Science*, available at <<http://www.fe.doe.gov/sequestration>>.

## 1. Geologic sequestration

The idea of sequestering CO<sub>2</sub> in geologic formations is relatively new. Beginning in the early 1990s, a number of key studies identified the fundamental concepts underpinning sequestration and identified three types of formations suitable for sequestration: (1) deep brine formations, (2) oil and gas formations, and (3) coal formations [1–18].

As the concept of geologic sequestration developed, it was recognized that CO<sub>2</sub> can be sequestered in geologic formations by three principal mechanisms [19]:

- (1) CO<sub>2</sub> can be trapped as a gas or supercritical fluid under a low-permeability caprock, similarly to the way that natural gas is trapped in gas reservoirs or that gas is stored in aquifer gas storage. This process is commonly referred to as hydrodynamic trapping and, in the short term, is likely to be the most important mechanism for sequestration.
- (2) CO<sub>2</sub> can dissolve into the fluid phase. This mechanism is referred to as solubility trapping. In oil reservoirs, this lowers the viscosity and swells the oil, which provides the basis for one of the more common enhanced oil recovery (EOR) techniques. The relative importance of solubility trapping depends on a large number of factors, such as the sweep efficiency of CO<sub>2</sub> injection, formation of fingers, and the effects of formation heterogeneity.
- (3) CO<sub>2</sub> can react, either directly or indirectly, with the minerals and organic matter in the geologic formations to become part of the solid mineral matrix. Formation of carbonate minerals such as calcite or siderite and adsorption onto coal are examples of mineral trapping.

The relative importance of these mechanisms depends on the type of formation used for sequestration. For example, in brine formations, solubility trapping is most important, at least in the short term. By comparison, in coal formations, much of the CO<sub>2</sub> adsorbs to the solid phase.

Several worldwide and national assessments of the storage volume available for sequestration demonstrate the significant potential for geologic sequestration of CO<sub>2</sub> in brine formations, coal formations, and depleted oil and gas reservoirs. Worldwide estimates range from 100 to 3,000 GtC [16]. In the U.S. alone, estimates range from 1 to 130 GtC for brine formations [15], 10 to 25 GtC for gas formations [20], and 10 GtC for enhanced coal bed methane production [21]. Since analysis of CO<sub>2</sub> storage potential in geologic formations is a relatively new field of study, some of these estimates may increase.

Sequestration in geologic formations is likely the first large-scale target for sequestration of CO<sub>2</sub> from point sources such as power plants or large industrial facilities—for a number of reasons:

- Industrial experience in the oil, gas, and gas-storage industry can provide the expertise and technology needed to enable rapid commercialization of this approach.
- Several collateral economic benefits are possible, including CO<sub>2</sub>-enhanced oil and gas recovery and enhanced coalbed methane recovery.
- Suitable geologic formations, including oil, gas, brine, and coal formations, are located across the U.S.
- The regulatory infrastructure associated with injection into oil and gas formations is well established, enabling rapid application of sequestration technologies in these types of formations.
- Geologic analogs such as natural CO<sub>2</sub> reservoirs prove that geologic structures can sequester CO<sub>2</sub> over very long times.
- Public acceptance for geologic sequestration will grow as technological advances lead to innovative methods for creating permanent mineral sinks for CO<sub>2</sub>.

Recent years have seen rapid progress in geologic sequestration. The Norwegian energy firm Statoil's Sleipner Vest project, the first CO<sub>2</sub> sequestration project in a brine formation, has now been underway for nearly 3 years [22]. Statoil has demonstrated that one million tonnes per year of CO<sub>2</sub> can be separated from natural gas produced in the North Sea and sequestered in a subsea brine-filled sandstone formation at a depth of 800 m. Progress is also being made in sequestering CO<sub>2</sub> in oil formations. This option is comparatively attractive because of the opportunity to offset the cost of sequestration by CO<sub>2</sub> EOR. Two demonstration projects are underway or in the planning phase. In October 2000, Pan Canadian Resources plans to begin injecting CO<sub>2</sub> separated from a coal gasification plant in North Dakota into the Weyburn Field, a fractured carbonate reservoir for EOR [23]. In addition, BP-Amoco is developing a demonstration project for CO<sub>2</sub> EOR on the North Slope of Alaska in the Schrader Bluff field, using CO<sub>2</sub> separated from gas-turbine exhaust gas [24]. Two pilot projects of enhanced coalbed methane production using CO<sub>2</sub> injection are also underway in North America, one in the San Juan Basin, New Mexico, and one in the Alberta Basin, Canada [21, 25].

While significant progress in geologic sequestration is being made, a number of issues must be addressed to make geologic sequestration more attractive:

**Lower the cost and energy requirements of geologic sequestration:** Cost estimates for geologic sequestration [16, 26] indicate that over 75% of the costs of geologic sequestration are associated with separation and capture, compression, and transportation, rather than the well-field operations themselves. Nevertheless, opportunities exist to lower the net cost of sequestration by optimizing the geologic sequestration system. Examples of these opportunities include: offsetting the cost of sequestration with value-added benefits such as enhanced oil recovery or enhanced gas recovery; lowering the overall cost by sequestering less pure CO<sub>2</sub> waste streams that are less expensive or require less energy to separate from flue gas; and minimizing

CO<sub>2</sub> transportation and compression costs by identifying sequestration sites that are close to the CO<sub>2</sub> generator.

**Identify and demonstrate reliable and cost-effective systems for monitoring CO<sub>2</sub> migration in the subsurface:** Monitoring CO<sub>2</sub> migration in the subsurface plays several diverse and critical roles in the development and acceptance of geologic sequestration. First, it is essential for accounting purposes. That is, it will be necessary to verify the net quantity of CO<sub>2</sub> that has been sequestered in the subsurface. Second, it is necessary for monitoring sweep efficiency and determining whether the available sequestration capacity is being used effectively. Third, it is needed for optimizing EOR and enhanced coalbed methane recovery. Finally, it is necessary to ensure the safety of sequestration projects by demonstrating that the CO<sub>2</sub> is retained in the formation into which it was injected. Monitoring approaches are likely to be crosscutting, with some level of refinement for the different types of formations. Methods are needed to assess all three trapping mechanisms: hydrodynamic, solubility, and mineral. Methods for monitoring hydrodynamic trapping are the best developed and build on decades of experience gained in the oil and gas industry. Significantly more R&D will be required to develop reliable methods for monitoring solubility and mineral trapping. Promising options for monitoring include: surface monitoring of rates and compositions of injected and produced gases and liquids; seismic and electromagnetic geophysical imaging techniques; reservoir pressure and temperature monitoring; and natural and introduced chemical tracers that will provide additional information needed to quantify hydrodynamic, solubility, and mineral trapping rates and processes.

**Enhance, develop, and verify subsurface transport models for predicting, assessing, and optimizing the performance of CO<sub>2</sub> sequestration in geologic formations:** Computational models that can be used to predict, assess, and optimize geologic sequestration are among the most important enabling technologies for geologic sequestration. Nearly three decades of industrial experience in the oil and gas, groundwater, gas storage, and environmental remediation sectors have led to the development of many models that are used routinely for predicting migration of fluids and gases underground. In practice, these models have been used with good success. The success of these models, however, is based on extensive calibration, history matching, and relevant experience from related applications. Developing reliable models for geologic sequestration will require similar levels of practical experience.

**Develop better capacity estimates and screening criteria for brine and coalbed methane formations to help CO<sub>2</sub> generators, sequesterers, and regulators identify formations that are suitable for sequestration on a regional basis:** Significant improvements in capacity assessment are needed to advance geologic sequestration. Worldwide estimates of the sequestration capacity of geologic formations are large, ranging from 100 to 3,000 GtC [16]. In the U.S., the range is also large and in need of refinement. Moreover, it is important not only to account for the storage volume available for sequestration, but also to determine what fraction of the available storage space will be occupied by CO<sub>2</sub>. This will depend strongly on the heterogeneity of the formation and the complex interplay of viscous and gravitational forces. For example, studies by van der Meer [6] suggest that only 1–6% of the storage volume in porous formations will be occupied with CO<sub>2</sub>. Additional site-specific and regional investigations are needed to refine capacity estimates. This should be accompanied by a systematic effort to

develop screening criteria that will help CO<sub>2</sub> generators, regulators, and the sequestration industry select the best sites for geologic sequestration.

**Engage the public:** Over the past several decades, we as a society have learned that engaging the public early and in a meaningful way is a prerequisite to the acceptance of new technologies, particularly those technologies with potential environmental or economic impacts. Without significant involvement, the public will neither understand the need for geologic sequestration nor willingly accept the costs and potential risks associated with it. A two-way exchange of information, options, and concerns will be needed to build the broad consensus needed for large-scale application of any form of carbon sequestration.

**Initiate additional pilot tests:** The need to begin additional pilot projects now has been a recurring theme throughout the R&D planning activities. Industry leaders, academic and national laboratory researchers, and federal research managers all agree that pilot testing, conducted with the full complement of scientific tools to predict, monitor, and verify performance and to assure public safety, is an essential next step. Unlike some of the other sequestration technologies that will require years to decades of fundamental and applied R&D before they are ready to be implemented, geologic sequestration is poised for early application. The experiences at Sleipner Vest, at Weyburn, and in the San Juan Basin attest to the practicality of this approach. A set of scientifically conducted and monitored pilot tests, in each of the different formations being considered for sequestration, is needed to sustain the momentum required to build confidence, accelerate development, and ready this technology for application.

## 2. Separation and capture of CO<sub>2</sub>

In numerous forums, separation and capture of anthropogenic CO<sub>2</sub> have consistently been ranked among the most critical technologies for achieving the overall goal of safe, long-term, environmentally acceptable sequestration of carbon. These technologies have the greatest potential to stabilize atmospheric CO<sub>2</sub> at a level where there is no discernable change in our global climate. Stabilizing CO<sub>2</sub> is critical because CO<sub>2</sub> is the dominant anthropogenic greenhouse gas (GHG). Although CO<sub>2</sub> is the least effective greenhouse gas on a molecular basis, its much higher concentration in the atmosphere (currently 365 ppm) gives rise to its large impact.

A major focus of the National Energy Technology Laboratory (NETL) program for the management of greenhouse gases is the development of a suite of technologies for the capture and separation of CO<sub>2</sub> at large point sources. These sources include power production, natural gas processing, oil refining, and a number of industrial activities. For example, electric power plants account for 36% of the CO<sub>2</sub> emitted in the U.S. Capture technologies need to be low cost, high impact (in terms of tons of CO<sub>2</sub> emissions avoided), safe, and environmentally sound. Both the capital and operating costs associated with capture and separation must be reduced.

In support of the program and under DOE leadership, researchers from universities, industry, other government agencies, and DOE national laboratories were brought together to develop the technical basis for conceiving a science and technology road map for carbon sequestration. The effort produced a report, *Carbon Sequestration: State of the Science*, which is available from the Office of Fossil Energy's web site at [www.fe.doe.gov/sequestration](http://www.fe.doe.gov/sequestration). In the chapter devoted to

separation and capture of CO<sub>2</sub>, current and potential science and technology requirements, capabilities, and gaps were identified. Elements of the NETL program that are beginning to address the identified needs or gaps (indicated by quotations) are summarized below.

**Need: ‘Currently, capital and energy costs are prohibitive for flue gas treatment to separate and capture CO<sub>2</sub>. It may be possible to develop novel solvents and contactors to reduce these costs. Prudent courses of action include investments in R&D on novel solvents, particularly those amenable to use in advanced systems, and investments in system studies to identify the best possible configurations of processes and equipment, particularly as they relate to cost and process simplicity’.**

To reduce energy losses and costs while producing concentrated hydrogen, NETL recently awarded a project that removes CO<sub>2</sub> from energy plant gas streams as an ice hydrate. The award was made to a research and development team led by Bechtel National, Inc., joined with Los Alamos National Laboratory and SIMTECHE.

Successful application of this innovative approach, first demonstrated by SIMTECHE, will help DOE reach its Vision 21 goal of 50% to 60% power-plant energy-conversion efficiencies with near-zero CO<sub>2</sub> emissions. Vision 21 is a DOE concept in which a fleet of highly efficient, fuel-flexible power plants would produce electricity along with a slate of energy products, such as clean liquids for transportation fuels, chemicals, and feedstocks, in response to regional energy markets.

The work involves removing CO<sub>2</sub> from a shifted syngas stream (a mixture of mostly CO<sub>2</sub> and hydrogen) in the form of a solid hydrate (an ice-like material) in a water slurry at near-freezing temperatures and high pressure. Before forming a hydrate, water is ‘nucleated’ using high-pressure CO<sub>2</sub> to form clusters of molecules ready to grab onto additional CO<sub>2</sub>, which further purifies the hydrogen gas. Continued hydrate formation takes place in a venturi reactor. The hydrate can be decomposed by temperature swing, theoretically using one-fourth of the energy of a typical amine regeneration. The purified hydrogen gas could be used in an integrated gasification combined-cycle (IGCC) power plant or combined with a fuel cell, which is a highly efficient way of producing electricity.

**Need: ‘Considerable interest has been shown in the concept of retrofitting conventional pulverized-coal boilers for CO<sub>2</sub> recycle to increase the CO<sub>2</sub> concentration to the point where recovery becomes economically feasible’.**

Capturing CO<sub>2</sub> from conventional pulverized-coal-fired power plants is currently very costly, in part because of its dilution in the flue gas and also because of the required pretreatment of the flue gas. One option to reduce the cost of gas separation is to increase the concentration of CO<sub>2</sub> in the flue gas. This can be achieved by increasing the oxygen in the feed gas and, eventually, by recirculating part of the flue gas. Coal combustion at higher oxygen concentration is particularly attractive because it not only reduces the cost of CO<sub>2</sub> separation in the flue gas, but it also reduces the volume of inert gas, increasing the boiler thermal efficiency.



Recirculation of the flue gas is needed when a very high CO<sub>2</sub> concentration in the flue gas is required. Concentrations up to 98% CO<sub>2</sub> in dry flue gas may be attainable, allowing CO<sub>2</sub> to be reused or stored with little or no extra treatment. Other advantages are the ability to minimize unburned carbon associated with the higher oxygen concentration and the expected reduction of NO<sub>x</sub> emissions. Japanese researchers have found that NO<sub>x</sub> emissions are lower during O<sub>2</sub>/CO<sub>2</sub> combustion and recycled combustion. They explain NO<sub>x</sub> reduction during recycled combustion by the fact that part of the recycled NO (actually more than 50%) is reduced to molecular nitrogen.

A pilot-scale experimental study is underway on O<sub>2</sub>/CO<sub>2</sub> recycle combustion by Natural Resources Canada at the CANMET Energy Technology Centre in Ottawa, Canada. A cylindrical, down-fired vertical combustor was chosen as the preferred method of fuel combustion. This reactor permits the establishment of axisymmetric flames that can be analyzed by water-cooled instruments and probes to evaluate the radial and axial profiles of in-flame gaseous and particulate species, temperature, and heat-transfer properties. The vertical combustor has a rated firing capacity of up to 0.3 MW and can burn solid, gaseous, and liquid fuels.

To complement the experimental study, Argonne National Laboratory is conducting an evaluation of the recovery of CO<sub>2</sub> from pulverized-coal-fired power plants retrofitted for flue gas recirculation. The full energy cycle will be considered, including mining, coal transportation, coal preparation, the PC-fired boiler with power generation, particulate removal and flue gas recirculation, pipeline CO<sub>2</sub> conditioning, and pipeline transport of CO<sub>2</sub> to sequestration. Process design conditions and costs will be estimated. Issues relating to CO<sub>2</sub> sequestration in a variety of host reservoirs will be surveyed.

**Need: ‘Systems that use air to support combustion present difficulties in separation and capture of CO<sub>2</sub> because of the large amount (~80%) of nitrogen diluent in the process stream’.**

TDA Research, Inc., is developing a ‘Sorbent Energy Transfer System’ in which a fossil fuel (gasified coal, oil, or natural gas) reduces a metal oxide, producing steam and high-pressure CO<sub>2</sub>. The steam is used to drive a steam turbine to produce electricity. The high-pressure CO<sub>2</sub>, free of nitrogen diluent, can be sequestered with little additional compression energy. The metal is then reoxidized in air, stripping out or absorbing the oxygen. A separate oxygen plant is not required. The oxidation raises the temperature of the high-pressure offgas, which powers a gas turbine to generate more electricity. The metal or oxidized metal is continuously cycled between two transport reactors that replace the combustor in an advanced power cycle.

To bring the SETS process to commercial reality, TDA is to (1) carry out the conceptual and thermodynamic analyses necessary to better define the cycle and optimize the reaction conditions, (2) develop a sorbent with suitable physical and chemical properties, (3) test the sorbent at the laboratory and pilot scale, (4) engineer the oxidation and reduction reactors, and (5) prepare detailed engineering designs to accurately predict the total cycle performance and cost.

**Need: ‘As a baseline case, the cost and energy benefits of chemical absorption processes integrated into an IGCC or other advanced power system must be demonstrated in a commercial setting as a real-case option’.**

Specific and significant opportunities exist within Tampa Electric’s (TECO’s) 250 MW Polk Power Station to recover CO<sub>2</sub> gas. The oxygen-blow integrated gasification combined-cycle power system is a near ideal platform for the production of concentrated CO<sub>2</sub> streams on a commercial scale. Recovered CO<sub>2</sub> would be used commercially to offset current refrigeration needs and for other local consumer products. TECO made a preliminary overall technical and economic assessment of three options: (1) the direct removal of CO<sub>2</sub> from the clean syngas, (2) CO<sub>2</sub> removal from an acid gas stream coming from the existing amine scrubber, and (3) the removal of CO<sub>2</sub> from an enriched-air-fired sulfuric acid plant stack. All options used conventional amine scrubbers. Further refinement of the economics needs to be done to move ahead towards benchmarking current technology. The project is currently on hold.

**Need: ‘Novel gas/liquid contactors must be developed to minimize mass- and heat-transfer effects in gas scrubbing’.**

A joint industry-INEEL (Idaho National Engineering and Environmental Laboratory) partnership is currently developing vortex contactor technology for natural gas liquids-related application. INEEL will develop and demonstrate the unique gas-liquid contactor for separating CO<sub>2</sub> from natural gas and flue gas. The objective is to achieve at least 50% improvement in performance and cost over conventional gas absorption technology for separating CO<sub>2</sub> from dilute mixtures (<15% CO<sub>2</sub>) by employing an operationally robust vortex tube contactor.

The work specifically addresses (1) CO<sub>2</sub> liquid absorption kinetics in a vortex reactor, (2) solvent throughput and regeneration requirements, and (3) scaled vortex-tube performance. The vortex-tube design and operation will be optimized to develop the necessary information for process scale-up and eventual field demonstration. The work builds on Ranque-Hilsh vortex technology, which has been used for many years for small cooling applications. There is significant cost sharing from industrial partners, including Pacific Gas and Electric, Southern California Gas, and BP Amoco.

**Need: ‘Other novel adsorption concepts for CO<sub>2</sub> separation and capture are likely, and R&D on novel concepts should be pursued’.**

Oak Ridge National Laboratory (ORNL) is developing an advanced approach, called electrical swing adsorption (ESA), that addresses many of the issues of pressure swing and temperature swing adsorption systems. ORNL is using a novel carbon-bonded activated carbon fiber as the adsorption medium. Activation conditions for these adsorbents may be varied to increase or decrease pore size, pore volume, and surface area to improve the effectiveness of the carbon fiber as a CO<sub>2</sub> adsorbent. This material is also highly conductive electrically, so adsorbed gases can be rapidly, effectively, and efficiently desorbed by passing a low-voltage electrical current.

This adsorption-desorption process may be used with no variation of system pressure and with minimal variation in system temperature. The electrical energy required for desorption is

approximately equal to the heat of adsorption of the adsorbed gas. Thus, the ESA process is promising as an energy-efficient, economical gas separation and capture method. The project is currently on hold.

**Need: ‘Considerable R&D is required to realize the potential of membranes for separation and capture of CO<sub>2</sub>, particularly at higher temperatures and pressures’.**

Los Alamos National Laboratory, in collaboration with the University of Colorado, INEEL, Pall Corporation, and Shell Oil Company, is developing a high-temperature polymer membrane that will exhibit a permselectivity an order of magnitude higher than current polymer membranes. Modified polybenzimidazole polymer membranes will be tested at temperatures from 100°C to 400°C to take advantage of enhanced gas diffusion and permeance at higher temperatures. In essence, the structure of the polymer will be ‘tuned’ to operate in an optimum temperature range with high selectivity. Functional sites will be placed in the structure to facilitate transfer of CO<sub>2</sub> through the membrane.

**Need: ‘Inorganic, palladium-based membrane devices could be developed that reform hydrocarbon fuels to mixtures of hydrogen and CO<sub>2</sub> and that, at the same time, separate the high-value hydrogen. The remaining gas, predominantly CO<sub>2</sub>, would be recovered in a compressed form’.**

Research Triangle Institute is using a novel ‘electroless’ (chemical) plating technique to produce ultrathin membranes. Electroless plating has the potential to yield thin films of palladium, which was the key barrier issue in past work. Palladium embrittlement is countered by alloying with silver, and a platinum overlay gives resistance to sulfide attack. The highly permeable palladium membranes require less surface area and smaller reactors, reducing capital costs. The shift reaction to produce hydrogen and CO<sub>2</sub> could be done in the same reactor using suitable catalysts. This shift reaction is driven to completion as hydrogen passes through the membrane with 100% selectivity. Carbon dioxide is recovered at high pressure, enabling easier long-term sequestration at less cost. Initial work has demonstrated that membranes are highly permeable and selective.

In addition, NETL is establishing a Center of Excellence in Carbon Sequestration. The President’s Council on Advanced Science and Technology recommended that the Office of Fossil Energy provide national leadership, recognized expertise, state-of-the-art facilities, effective partnerships, and stakeholder support to meet future challenges for energy technologies. Thus, the Center of Excellence will build on in-house research capabilities and successes and will accelerate the ongoing revitalization of facilities at NETL. Specifically, a versatile capture facility will be constructed for testing various capture technologies. Work has also begun on two research projects, ‘Optimizing Chemical Scrubbing Processes for CO<sub>2</sub> Separation’ and ‘CO<sub>2</sub> Scrubbing with Regenerable Sorbents’.

In the first project, technical and economic improvements in wet scrubbing of CO<sub>2</sub> from flue gas, as compared to conventional techniques, will be determined. Various solvents will be identified that are better than the conventional solvents used for CO<sub>2</sub> scrubbing. Parameters that optimize the performance of the solvent will be identified. The objective of the second study is to identify potential regenerable sorbents that could be used for the capture of CO<sub>2</sub> from a gas stream, and to

validate a potential dry, regenerable sorbent process capable of removing CO<sub>2</sub> from a gaseous stream. It is known that metal carbonates/bicarbonates can be used for this purpose.

The NETL carbon sequestration program is addressing many issues identified in the *Carbon Sequestration: State of the Science* report. We will continue to expand the program to address other identified needs and to ensure that a suite of cost-effective technologies becomes available to address the long-term issue of global climate change. The scientific community is being asked to participate through a series of solicitations issued by NETL. An example is the Program Solicitation for Financial Assistance Applications for ‘Research and Development of Technologies for the Management of Greenhouse Gases’, on the NETL website at <http://www.netl.doe.gov/business>.

### 3. Advanced concepts for CO<sub>2</sub> reuse or sequestration

The concentration of CO<sub>2</sub> in the Earth’s atmosphere has increased significantly over the last fifty years. In the next fifty years, projected increases in energy use by developing countries will exacerbate this problem as more fossil fuels are converted to CO<sub>2</sub>. This trend demands that carbon resources be managed more efficiently and aggressively. Increases in energy efficiency will help mitigate but not eliminate the problem, and the low energy-density and high cost of alternative energy sources suggest we will continue to depend on fossil fuels well into the 21<sup>st</sup> century. Carbon sequestration can significantly contribute to reversing the trend of increased atmospheric carbon dioxide (cf. *Scientific American*, February 2000).

In DOE’s *Carbon Sequestration: State of the Science* report, advanced carbon sequestration concepts were identified as a major component of a national effort. Similarly, the Carbon Sequestration Program Strategy of the Office of Fossil Energy within DOE places great emphasis on fostering advanced concepts. Previous discussions of advanced process concepts for carbon sequestration focused on several issues. Does the term *advanced concepts* refer to process concepts that would be commercialized later (say, 2015–2020) in a carbon management strategy or, alternatively, unanticipated ideas that might be commercial within as few as five years? How safe, reliable, environmentally secure, and cost effective are the advanced ideas we have found and hope to find? Other factors that must be considered are the transition of the technology system and possible changes in the values that are important in society that occur over time. It is important to recognize that the slate of technologies that will find commercial success twenty years from today may be quite different from those of today. The way people work and live (and their expectations for the future) in 2020 may point to a unique target for advanced process concepts. Therefore, any discussion of advanced concepts raises questions not just about the concepts but about our vision of the future.

Furthermore, work done on advanced chemical and biological concepts may benefit other approaches to sequestration. Perhaps the largest impact could be achieved in terrestrial carbon sequestration from improvements in plant photosynthesis and stress tolerance. Improved ocean and soil algal and microbial processes also have potentially significant impacts. Volume reduction for storing liquid and solid CO<sub>2</sub>-derived products can productively impact geologic sequestration. Chemical trapping and concentration can be accomplished with reversible organic

processing, and biological processes can use impure and dilute CO<sub>2</sub>-containing streams. This is a high-impact advantage in that separation and capture processes add significant cost to any process that requires essentially pure carbon dioxide. We also note that analytical chemistry methodologies may provide techniques to meet the overarching need for monitoring and verifying carbon sources and sinks.

Examples of advanced process concepts focused solely on sequestration could include:

- Creation of novel manufactured products from captured CO<sub>2</sub> with large potential 'markets'
- Direct capture of CO<sub>2</sub> from the air
- Use of CO<sub>2</sub> to manufacture polymers that are currently in wide commercial use
- Capture of CO<sub>2</sub> in magnesium-containing materials to form magnesium carbonates
- Produce ammonium bicarbonate (NH<sub>4</sub>HCO<sub>3</sub>) fertilizer from water, ammonia and carbon dioxide
- Increase plant enzyme activity for carbon (rubisco, PEP carboxylase) and nitrogen fixation (nitrogenase) pathways to increase biomass yields
- Modify plants to produce more durable or cost-competitive carbon-based materials.

An additional category emphasizes the fact that capture technologies may be integrated into energy production schemes that bring together sequestration and other forms of carbon management:

- Use supercritical CO<sub>2</sub> to form man-made geothermal hot-rock reservoirs and as the heat-transfer fluid in geothermal power plants.
- Develop offshore energy complexes that generate power from undersea resources and return captured CO<sub>2</sub> to undersea formations.

The need remains to develop a working definition of advanced/novel sequestration concepts. Such concepts will enable us to apply appropriate means to assess all risks associated with moving from good ideas to commercially viable processes. Differences in the state of development between a simple extension of current knowledge and a thorough investigation of an advanced concept (possibly requiring significant technological breakthroughs) make comparisons problematic. A hallmark of advanced process concepts is the level of technical risk, as opposed to financial risk, that exists.

Another overarching requirement for any of these processes is an accurate understanding of the environmental impacts with respect to products, byproducts, lifetimes of both, and their dispersal into the environment. The term *dangling impacts* was used to describe unanticipated, long-term

effects. One approach is to use a ‘rough’ environmental impact filter for a proposed process in which upstream and downstream impacts can be assessed from the beginning. An example is what happens to produced  $\text{MgCO}_3$  in the carbonation of minerals concept: is it reburied, left on the ground, or used in some way? Such a combined risk assessment (technical, environmental, and financial—assuming that externalities are captured in the methodology) must be incorporated in proposed approaches to carbon sequestration.

As a consequence of the roadmapping process to date, we have developed a number of concepts and a set of questions that may be used to ask whether a concept fits into this category.

### **What objectives do we set for technologies that might emerge?**

Four key objectives were defined:

- Develop breakthrough processes with the potential to sequester large amounts of carbon dioxide ( $\text{CO}_2$ ) and other GHGs with sequestration lifetimes greater than 100 years.
- Develop value-added products from GHGs as opposed to storing it in a relatively inert and unusable form. This approach captures the idea that  $\text{CO}_2$  can be used as a feedstock to produce useful products.
- Create new tools, concepts, and information that expand our ability to develop sequestration options and understand their respective impacts on environmental systems.
- Develop key subprocesses that enhance other sequestration options (i.e., geological, terrestrial, oceans). An example is to condense gaseous  $\text{CO}_2$  into liquid (microbial process to convert  $\text{CO}_2$  to water-soluble acetate) or solid forms of carbon to reduce containment volumes or increase capacities of geological repositories.

### **How do we investigate such concepts while recognizing that standard methods of evaluation, including economic analyses, may not provide a useful picture of the potential but merely focus on current shortcomings? How do we factor in the evolution of technology across society?**

- Focus research and development priorities on identifying high impact approaches that have long product (sequestration) lifetimes and byproducts that are well characterized in terms of future chemical changes, potential toxicity of products and their derivatives, and dispersal into the environment.
- Look towards 2030 and collect the ‘low-hanging’ fruit in transit by focusing on revolutionary rather than incremental processes that can transform the approaches to carbon sequestration.

- Consider CO<sub>2</sub> as a resource for providing products in a value-added sequestration approach in addition to considering CO<sub>2</sub> as a more traditional storage issue
- Consider a product versus process approach in which large impact products are identified and processes are developed to make them
- Explore means to optimize the possible reduction in greenhouse gas emissions by linking sequestration technologies and carbon management options. Recognized that many of the concepts include both sequestration and management opportunities and should be judged from an integrated perspective.
- Develop life-cycle analysis capabilities for evaluating total carbon emissions and energy requirements. The idea is that a coarse filter is applied in which a proposed process is evaluated for net CO<sub>2</sub> emissions.

In summary, how far into the future can we look from a technology development perspective when dealing with an issue as large as carbon sequestration? Achieving atmospheric stabilization of CO<sub>2</sub> will require many decades, perhaps a century or more of effort. Contributions to a technology-driven solution that are made available in the first half of this century will have impacts, positive or negative, for many years to come. Should we focus on the period from 2015 until 2025? Until 2050? How does one aggressively pursue innovation in an area such as this but still subject concepts to appropriate levels of critical analysis to explore their continuing relevance?

#### **4. Sequestration in terrestrial ecosystems**

##### **What is carbon sequestration in terrestrial ecosystems?**

Carbon sequestration in terrestrial ecosystems is defined as the net removal of CO<sub>2</sub> from the atmosphere into long-lived pools of carbon. The pools can be living, aboveground biomass (e.g., trees), products with a long, useful life created from biomass (e.g., lumber), living biomass in soils (e.g., roots and microorganisms), or recalcitrant organic and inorganic carbon in soils and deeper subsurface environments. It is important to emphasize that increasing photosynthetic carbon fixation alone is not enough. This carbon must be fixed into long-lived pools. Otherwise, one may be simply altering the size of fluxes in the carbon cycle, not increasing carbon sequestration.

Currently it is estimated that the terrestrial biosphere is a net sink for approximately 2 GtC/year. The estimated total amount of carbon stored in terrestrial ecosystems is approximately 2,500 GtC [27]. The challenge for sequestration in terrestrial ecosystems is to optimize the balance among the use of available land area, vegetation (and its use), and the longevity of belowground carbon in soils. Discovering an environmentally acceptable way to increase the long-lived carbon stocks by only 0.1% each year would sequester 2.5 GtC per year—a substantial contribution of current global emissions (~7.4 GtC/year).

## **What approaches can be used to enhance carbon sequestration in terrestrial ecosystems?**

There are two approaches to increasing carbon sequestered by terrestrial ecosystems: (1) using existing methods protect current inventories and recover some of the carbon lost over years of poor land-use practices and (2) discover (through research) new or improved ways to manage ecosystems that promote increased carbon storage. (This approach will be discussed in later sections.) For the first approach, there are many examples of what can be accomplished. For example, The Nature Conservancy [28] has projects for protecting forests in South America that will protect and increase carbon inventories at an estimated cost of only ~\$10 per ton of carbon. Protection of soils, which contain ~75% of all terrestrial carbon, is another practice that should be implemented aggressively now. The Conservation Reserve Program in the United States has been promoting protection and enhancement of soil carbon for many years. Additional practices (e.g., reforestation, promotion of agro forestry) can be implemented now to recover some of the 40 to 60 Gt of carbon that have been lost from soils since the agricultural expansion of the 1800s. One cautionary note is required, however. Management practices must be implemented to minimize carbon costs that would offset the sequestration credits. For example, use of inorganic fertilizers increases CO<sub>2</sub> emissions through their manufacture. Also, altering land-use patterns can potentially increase the release of other greenhouse gases (e.g., grasslands releasing N<sub>2</sub>O and wetlands releasing methane). Therefore, it is important to perform complete life-cycle carbon (or emission equivalents) accounting when considering any practice.

## **What is the potential for carbon sequestration in terrestrial ecosystems?**

Estimates of the potential for increased carbon sequestration from implementing accepted management practices vary widely and are highly uncertain at this time. For the U.S., estimates for total sequestration from forest, crop, and pasture management range from 0.3 to 0.8 GtC/year averaged over the next 20–50 years. Globally, typical estimates range from 2 to 5 GtC/year averaged over the next 100 years. These values assume improvements in agricultural, forestry, and land-use practices. They do not, however, assume any breakthroughs from research targeted at the problem.

The U.S. Department of Energy has released a report on the state of sequestration science [29]. In the chapter on terrestrial ecosystems, they suggest that with breakthroughs from research, sequestration rates of up to 10 GtC/year might be achievable. They also correctly caution that such high rates may not be sustainable over long periods of time. In addition, other issues need consideration: the increased rates must be net rates, after accounting for the energy costs (emission equivalents) to manage large areas of ecosystems. The environmental consequences of pushing ecosystems toward maintaining larger and longer-lived pools of carbon must be evaluated. Carbon sequestration will need to occur in a global environment of increasing atmospheric CO<sub>2</sub> concentrations and changing climatic conditions. Therefore, understanding the current fluxes of CO<sub>2</sub> and the complex dynamics of ecosystems must remain a research focus. Otherwise, strategies might be implemented that will fail as environmental conditions are altered by rising emissions of CO<sub>2</sub>.



## **How can one achieve the potential carbon sequestration?**

Enhancing carbon sequestration in terrestrial ecosystems requires the management of lands at the scale of landscapes to regions. Otherwise, the impact is not significant. Present ecosystem management practices typically focus on the production of a commodity (e.g., wood, forage, grain). If done properly, these practices may aid carbon sequestration, but they may also limit the potential for total system carbon storage. Many strategies to increase carbon sequestration over the next 20–50 years will focus on the pools of carbon with lifetimes of 10–100 years. These intermediate-lived pools include both portions of the soil carbon and the above biomass converted into long-lived products. Short-lived pools such as unused aboveground biomass or active fractions of soil carbon are usually small and turn over rapidly (months to a few years). Ideally, strategies would focus on the long-lived pools of soil carbon with residence times of 100 to 1,000 years. However, little is known about the potential to increase the size of this pool in a given soil.

## **How can science support the development of strategies for carbon sequestration in terrestrial ecosystems?**

One of the major research challenges must focus on the soil carbon pool. This is the largest pool of carbon in terrestrial ecosystems and can be long-lived. The challenge is to discover the critical links and pathways among larger, longer-lived pools as well as the manipulations or management strategies that impact the ecosystems at landscape to regional scales. Fundamental understanding of physiological, microbial, and interfacial processes responsible for increasing the size and lifetime of soil carbon pools is critical to support the development of management strategies that can be implemented at large scales. To gain this understanding will require research at all scales, from molecular to landscape.

In 1999, the U.S. Department of Energy's Office of Science initiated a new center for research on enhancing carbon sequestration in terrestrial ecosystems (CSiTE). CSiTE is a research consortium among national laboratories (Oak Ridge, Pacific Northwest, and Argonne), universities (Colorado State, North Carolina State, Ohio State, Texas A&M, University of Washington), and research organizations (Rodale Institute in Pennsylvania, Joanneum Research Institute in Austria, and the U.S. Department of Agriculture labs). CSiTE targets scientific and technological advances that will yield long-term benefits to enhance carbon capture and long-term sequestration as one part of a carbon management strategy. The research focuses on determining mechanistic processes across multiple scales (molecular to the landscape) for several important ecosystem types (forest, grassland, agricultural). The scientific results support improving estimates of carbon sequestration potential for the U.S. and assessing environmental impacts and economic implications of carbon sequestration.

CSiTE multiscale research emphasizes: (1) understanding whole-system (plant and soil) carbon storage responses to management in various ecosystems, (2) determining the molecular-scale mechanisms responsible for carbon partitioning among pools and the protection of those pools as they are influenced by management, (3) quantifying effects of microbial community structure and function, especially the ratio of bacteria to fungi, on the recalcitrance of soil carbon, and (4) relating management practices to soil organic matter partitioning among alternative pools and

soil organic matter transport. Research at the landscape scale uses existing data from remote sensing to develop new approaches for characterizing existing carbon stocks and soil nitrogen availability. These approaches can identify key properties that correlate with the greatest potential for influencing carbon sequestration through management. Research at the ecophysiological scale evaluates existing data and makes new measurements of plant and soil carbon changes associated with forest nutrient management, with low-input cropping systems, and with grassland restoration from croplands. Data are used both to calibrate existing ecosystem models and as input to both landscape and integrated assessment models. Research at the molecular/interfacial scale provides a mechanistic understanding of how microbial and interfacial processes influence partitioning of carbon to labile, recalcitrant, and soluble pools (under different ecological conditions and management practices). This research provides explanations of results at the ecophysiological scale. It also provides new understanding of carbon partitioning mechanisms (e.g., inorganic carbon formation, movement of soluble carbon) that may reveal previously undiscovered pathways to be exploited in carbon sequestration. Integrated assessment research in CSiTE uses results of the scientific endeavors to improve models of carbon sequestration in terrestrial ecosystems, predict environmental impacts of carbon sequestration, and evaluate economic considerations in promoting behaviors that will support sequestration.

### **What other types of activities are currently going on elsewhere?**

Carbon sequestration as a partial solution to the problem of increasing CO<sub>2</sub> emissions is not a new concept [30], but it has gained more emphasis in recent years. Many studies and assessments of carbon sequestration are being conducted. As discussed earlier, there are activities that can be implemented now as well as new research that needs to be conducted to make sequestration in terrestrial ecosystems a viable option. Both types of activities are important in contributing to our understanding of carbon sequestration. As an example of practices that promote protection of carbon, TransAlta Corporation of Canada agreed in 1999 to purchase up to 2.8 million metric tons of carbon-emission reduction credits from farms in the U.S.—the largest such transaction ever [31]. The estimated cost was \$0.40 to \$3.00 per ton of carbon, and the future market might be hundreds of millions of tons. A new research foundation, BIOCAP CANADA [32], will explore how the biosphere in Canada can be used to manage GHG emissions and relieve the demand for fossil fuels. Carbon sequestration is one important component of this new integrated research framework. The International Soil Reference and Information Center [33] has performed a recent assessment of options for increasing carbon sequestration in soil.

### **What are some future needs should carbon sequestration become a viable option?**

For sequestration in terrestrial ecosystems to help mitigate CO<sub>2</sub> emissions, advances will be needed in estimating changes to carbon stocks. These estimates can be accomplished in two ways. One method would use ‘rules of thumb’ based on observable practices at the landscape scale. Development of such rules and validation of their accuracy and feasibility needs to be accomplished. Depending on the future need for more quantifiable methods, new sensors and measurement techniques may be needed for both aboveground and belowground carbon stocks. Currently, changes in belowground carbon are not detectable except after many years. The methods are also labor intensive and are unable to account for the heterogeneity of subsurface

systems. Therefore, *in situ* nondestructive sensors to quantify rates and limits of carbon sequestration over large areas may be required.

## 5. Ocean CO<sub>2</sub> sequestration

Society needs to understand the options available for controlling levels of atmospheric carbon dioxide. If we wait until the threat of CO<sub>2</sub>-induced harmful climate change becomes real, it could be too late to develop large-scale solutions to the problem.

About one-third of CO<sub>2</sub> (2 Pg C/yr of 6 Pg C/yr) we emit is already being sequestered by the oceans. This process is largely driven by the increasing over pressure of atmospheric CO<sub>2</sub> relative to the ocean as a result of CO<sub>2</sub> emissions; however, the long-term effects of this continuing process are unknown. Once in the ocean, both movement of water masses and the ocean's biological pump act to move carbon into the deep sea; the latter process is most important in moving carbon across isopycnals (e.g., downward through the stratified layers of the ocean). Key to predicting the impacts and efficacy of carbon sequestration in the ocean is the correct simulation of both physical and biological oceanographic processes; effective simulations are dependent on adequate ocean observations and correct parameterization of important processes.

The biological pump is the net downward transport of carbon through food-web processes (photosynthetic production of organic matter from dissolved inorganic carbon and nutrients in surface waters, grazing of the organic matter by zooplankton, downward rain of organic debris and/or downward biomass migration, with subsequent remineralization/respiration of the organic carbon back to inorganic carbon at depth). This natural carbon sequestration process not only affects the levels of CO<sub>2</sub> in the atmosphere but also structures the organic and inorganic pools of C, N, P, O, and many other chemical species in the oceanic water column. One model simulation has shown that atmospheric CO<sub>2</sub> would rise by over 150 ppmv without an operating biological pump [34]. Current estimates indicate that the biological pump is 10–20% efficient at moving photosynthetically fixed carbon below 100 m, and only several percent efficient below 1,000 m.

The oceans contain approximately 50-fold more carbon than the atmosphere and therefore could play an important role in carbon sequestration. Although marine plant biomass equals approximately 0.05% of terrestrial biomass, marine organisms photosynthetically fix an amount of carbon equal to that fixed by terrestrial plants (~50–100 Pg C/y). This seeming paradox is explained because marine plant biomass turns over on a time scale of hours to days, rather than seasons to years for terrestrial biomass. This fact makes monitoring the variability of efficiency and linkages of the biological pump with depth a major oceanographic challenge. Given the huge amounts of carbon flowing through the biological pump on an annual basis, perturbations of the pump's transport efficiency could have a huge impact on carbon sequestration rates.

Both the biological and physical pumps may be changed in this century. Coupled atmosphere ocean simulations suggest that anthropogenic emissions of CO<sub>2</sub> will lead to increased stratification in the upper ocean and a lowered surface pH [35]. Both effects would reduce the efficiency of both pumps, thereby leaving a larger fraction of anthropogenically produced CO<sub>2</sub> in the atmosphere. Understanding and quantifying the factors controlling sequestration efficiency

and ecological consequences requires both expanded observational information and better coupled 3-D time-dependent biogeochemical/ecosystem models.

There are two major proposed strategies for ocean carbon sequestration: (1) *enhancement of the biological pump* by ocean fertilization (hoping to increase the downward flux of organic carbon through increases of productivity and/or increases in biological pump efficiency) and (2) artificial delivery of CO<sub>2</sub> to deep waters by *direct injection* (a process that avoids the biologically rich surface layer altogether). Both strategies raise issues regarding (1) environmental impacts (i.e., whether impacts on oceanic ecosystems will, in the long run, cause more significant environmental problems down the road), and (2) feasibility and effectiveness (i.e., whether it can be done technically and whether the amounts of carbon that would be sequestered would be significant). Evaluation of these options must be made both in the context of the impacts of unchecked increase of anthropogenic CO<sub>2</sub> in absence of sequestration efforts, and relative to other sequestration options.

Research goals are (1) to improve the science base needed to understand basic biological, chemical, and physical processes relevant to ocean carbon cycle dynamics, (2) to use this improved science base to produce the best quantitative predictions of impacts of various sequestration approaches, and (3) to test and evaluate these predictions using additional experiments, observation, and monitoring. Current science and technology gaps are summarized below.

### **Direct Injection Science and Technology Gaps**

- **Injection Strategy**  
Evaluation of environmental impacts. Strategies to achieve longest sequestration. Deep versus mid-depth injection.
- **Engineering**  
Injection technology. Monitoring technology. Experimental demonstration of behavior of CO<sub>2</sub> at injection point. Understanding hydrate formation and dissolution. Defining strategies to involve carbonate sediments to minimize pH excursions.
- **Environmental Effects**  
Baseline measurements of carbon system. Evaluation of the consequences of doing nothing (e.g., CO<sub>2</sub> impacts at surface). Develop parameters of injection to minimize impacts. Understand effects of sustained release on ocean biogeochemistry and ecosystems. Define requirements for the purity of injected stream. Understand the role of bioturbation and neutralization of CO<sub>2</sub> by carbonate sediments.
- **Improve Ocean GCMs**  
Address weakness of ocean GCMs near boundaries. Develop hierarchy of models to address near field to far field effects. Model–model intercomparisons. Simulation of point source releases. Model–data intercomparisons.

- Pilot Experiments

Demonstrate feasibility of approach. Evaluate ecological Impacts. Obtain time series data.

## **Fertilization Science and Technology Gaps**

- Effects of Long-Term Fertilization on Function of Marine Ecosystem

Requires long term experiments (3-6 months). Phytoplankton species changes (and associated changes in DMS production). Food web changes. Positive (e.g., Fisheries enhancement) vs. negative effects (e.g., toxic algae?). Relationships of Fe and nitrogen fixation (cyano bacteria).

- Changes in Biogeochemical Cycles.

C (org), CaCO<sub>3</sub>, N, P, S, Si, Fe interrelationships are poorly known. Changes of export and remineralization? Anoxia in water column and sediments? Effects on carbon remineralization and preservation. Methane production?

- Ocean GCM Simulations.

Improvements in simulation of boundary effects. Biogeochemical process parameterizations (replace 25 cent biology). Remineralization efficiency parameterizations. Validation against real-world data. Sequestration effectiveness.

- Natural Carbon Cycle Observations

Identify the factors regulating the biological pump on a global scale. Observations in upwelling regions. Observations in dust affected areas (natural Fe deposition). Pools and fluxes of particulate and dissolved organic and inorganic carbon and related species.

- Technology

Cost-effective autonomous methodologies for precise and accurate carbon system observations. Fertilizer design to minimize impacts.

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