



**Novel Approaches to Carbon Management:  
Separation, Capture, Sequestration, and Conversion  
to Useful Products - Workshop Report**  
Committee on Novel Approaches to the Management of  
Greenhouse Gases from Energy Systems, National  
Research Council

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# NOVEL APPROACHES TO CARBON MANAGEMENT

## Separation, Capture, Sequestration, and Conversion to Useful Products WORKSHOP REPORT

Committee on Novel Approaches to the Management of Greenhouse Gases from Energy  
Systems  
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Division on Engineering and Physical Sciences  
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The Committee on Novel Approaches to the Management of Greenhouse Gases from Energy Systems wishes to acknowledge and thank the many individuals who participated in the National Research Council (NRC) Workshop on Novel Approaches to Carbon Management held in Irvine, California on February 12–14, 2003. These individuals, all of whom made valuable contributions in the form of discussions or presentations, are listed in [Appendix A](#). Their input is the basis for the workshop report that the committee has prepared.

The committee wishes to thank Scott Klara and Michael Knaggs, National Energy Technology Laboratory, for their presentations and discussions with the committee and workshop participants and for responding to requests for information by the committee.

Finally, the chairman wishes to recognize the committee members and the staff of the Board on Energy and Environmental Systems and the Board on Earth Sciences and Resources of the NRC for their hard work organizing and planning committee meetings and their individual efforts in gathering information and writing sections of the report.

This report has been reviewed in draft form by individuals chosen for their diverse perspectives and technical expertise, in accordance with procedures approved by the NRC's Report Review Committee. The purpose of this independent review is to provide candid and critical comments that will assist the institution in making its published report as sound as possible and to ensure that the report meets institutional standards for objectivity, evidence, and responsiveness to the study charge. The review comments and draft manuscript remain confidential to protect the integrity of the deliberative process. We wish to thank the following individuals for their review of this report:

Jay Ague, Yale University;

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James G.Ferry, Pennsylvania State University; and

John R.Wise (NAE), Mobil Research and Development Company, retired.

Although the reviewers listed above provided many constructive comments and suggestions, they were not asked to endorse the conclusions or recommendations, nor did they see the final draft of the report before its release. The review of this report was overseen by H.M.Hubbard, retired president and CEO, Pacific International Center for High Technology Research. Appointed by the National Research Council, he was responsible for making sure that an independent examination of this report was carried out in accordance with institutional procedures and that all review comments were carefully



considered. Responsibility for the final content of this report rests entirely with the authoring committee and the institution.

Dale F. Stein, *Chair*

Committee on Novel Approaches to the Management of Greenhouse Gases from Energy Systems

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# 1

## Introduction

The National Research Council's (NRC's) Committee on Novel Approaches to the Management of Greenhouse Gases from Energy Systems held a workshop at the Arnold and Mabel Beckman Center in Irvine, California, on February 12–14, 2003, to identify promising lines of research that could lead to currently unforeseen breakthroughs in the management of carbon from energy systems. The information identified by participants in the workshop will be used by the U.S. Department of Energy's (DOE's) Office of Fossil Energy (FE) to award grants for new research in carbon management.

During the workshop, invited participants from a variety of disciplines contributed their expertise and creativity to addressing the problem of carbon management. The ideas developed during the workshop were synthesized into this report by the committee,<sup>1</sup> which oversaw the organization and execution of the workshop. However, this workshop summary does not contain any committee conclusions or recommendations, but simply reports on research areas that were identified as promising during the workshop discussions.

The purpose of the workshop, as noted, was to identify novel approaches to the management of carbon from energy systems. Current global emissions of carbon from energy use amount to several gigatons of carbon (GtC) per year. To develop new approaches to managing these carbon emissions, the NRC assembled participants who had not necessarily been engaged in research on carbon management but who were able to creatively apply their knowledge to new fields. Approximately 70 participants were invited from the private sector, universities, DOE, other federal agencies, and other institutions, as well as from the memberships of the National Academy of Sciences and the National Academy of Engineering (see [Appendix A](#) for the list of participants). All participants other than committee members will be free to apply for DOE grants to pursue research explored at the workshop, but the intention to apply was not a prerequisite for attendance.

Participants assembled with the common goal of finding new approaches to reducing the net input to the atmosphere of carbon dioxide (CO<sub>2</sub>) from fossil-fuel-based energy systems. Areas of focus included attention to reducing emissions from fossil-fueled systems based on coal, oil, or natural gas; biological engineering approaches to removal of carbon from the atmosphere; engineering of the entire fuel-cycle system; and geochemical and other approaches to storing carbon.

Following the plenary session, which included overviews of the status of carbon management research and opportunities (see the workshop agenda in [Appendix B](#)), the workshop participants were divided into four subgroups on the following topics:

1. Advanced separations techniques,
2. Advanced subsurface technologies,
3. Advanced geochemical methods, and

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<sup>1</sup> The NRC's Board on Energy and Environmental Systems (BEES) and Board on Earth Sciences and Resources (BESR) formed the committee to conduct a number of activities to help DOE enhance its current and future efforts in seeking novel approaches to the management of greenhouse gas emissions from energy systems.

4. Novel niches—that is, various concepts (including biological) for converting CO<sub>2</sub> to useful products, among other ideas.

For the most part, the sessions were roundtable discussions, with individuals contributing ideas throughout the session.

The workshop is part of a project conducted by the NRC for DOE's Office of Fossil Energy (DOE/FE). DOE/FE will consider the workshop report as it develops a solicitation to be issued in spring 2003. The solicitation will call for research proposals on enabling science and technology research on novel approaches for the management of carbon from energy systems.

Once proposals are received in response to the solicitation, this committee will hold a meeting to review the proposals and will evaluate them on their scientific, technical, engineering, and environmental merits, among others. It will then write a letter report to DOE/FE on its evaluation of the proposals. After DOE/FE has received the letter report and issued its funding decisions, the committee will hold a meeting to identify lessons learned from the process used to elicit this first round of “novel exploratory research” proposals, and it will review DOE/FE's carbon management program (Carbon Sequestration Program) to consider priorities, balance, and project management. The committee will then write a short final report commenting on the program as a whole and on ways for DOE/FE to capitalize on the lessons learned.

Chapters 2 through 6 of this report summarize the most promising new ideas on carbon management identified by each of the four subgroups at the workshop. In the respective chapters, the ideas are described, their significance is explained, and research opportunities are listed. Each chapter includes a statement of the scientific and engineering challenges related to its topic. Chapter 6 includes crosscutting issues not specific to one of the four subgroups. The chapters themselves do not include detailed analysis regarding feasibility, energy and mass balance, and so forth, as the workshop's time and scope did not permit this; it is assumed such analyses will be carried out in the research proposals that DOE funds.

## 2

### Advanced Separations Techniques

The workshop sessions on separations techniques were aimed at identifying novel materials and process concepts for CO<sub>2</sub> and hydrogen production. The streams from which these gases need to be separated include low-pressure flue gas from the combustion of fossil fuels, and high-pressure streams from the gasification of fossil fuels, in addition to the separation of CO<sub>2</sub> from the atmosphere. Hydrogen was included because efficient and cost-effective purification methods, when coupled with low CO<sub>2</sub> emission generation methods, could enable wide applications of H<sub>2</sub> as fuel. Purification of oxygen was also on the agenda, but no notable ideas were presented.

At the present time, technology exists for the separation of CO<sub>2</sub> and hydrogen, but the capital and operating costs are very high, particularly when existing technology is considered for fossil fuel combustion or gasification streams. This limitation applies to all available separation schemes—to absorption by a liquid, adsorption by a solid, or separation by selective transport through a membrane. At the fundamental level, the high cost for all of these schemes results from two key factors: (1) the low mass fluxes in the separation units and (2) the high energy consumption during regeneration of the separation agent and/or the production of a high-pressure stream of CO<sub>2</sub> or hydrogen. The cost of the separation agents, their operating life, their selectivity, and the complexity of the process are also important factors in making any process economically attractive. High mass flux (reduced capital cost) and low energy consumption are key features that will make any novel material or process concept attractive and worth investigating. During the workshop sessions, many potential areas of research in advanced separations techniques were discussed at length. The following eight were considered to have promise and are discussed in the sections below:

1. CO<sub>2</sub> absorbents;
2. CO<sub>2</sub> sorbents;
3. Nanoscale materials as separation agents;
4. High-temperature membranes;
5. Electrochemical approaches for gas separations;
6. Small-scale widely distributed CO<sub>2</sub> recovery processes;
7. Carbon management through carbon monoxide; and
8. Novel hydrogen storage concepts.

#### CO<sub>2</sub> ABSORBENTS

Current commercial processes for CO<sub>2</sub> absorption utilize either the chemical interaction between CO<sub>2</sub> and a compound (e.g., amine, alkali metal hydroxide) or the physical interaction with a solvent (e.g., alcohol, ether). In either case, CO<sub>2</sub> is removed from the gas stream into the sorbent at a lower temperature or higher pressure and is later released at a higher temperature or lower pressure. Although absorption by chemical interaction is efficient, the process suffers from high energy consumption and degradation of the sorbent due to other contaminants (such as sulfur compounds and trace metals) in the flue gas and

decomposition in the case of amines. Physical solvent absorbents also degrade for similar reasons and suffer loss due to evaporation. There is need for new, low-cost sorbent materials that have enhanced stability, are less volatile and less viscous, have higher CO<sub>2</sub> capacity per unit of mass, are more environmentally friendly, and require less energy consumption for operation.

Potential candidate materials include but are not limited to the following: molten metal oxides, medium-temperature eutectics, ionic liquids, biphasic materials, and CO<sub>2</sub> transfer agents that reversibly form compounds with CO<sub>2</sub> (e.g., alkyl carbonate). Some of these materials offer the potential advantages of being stable above 300 °C, are nonvolatile, and have tunable properties. Hybrid materials that possess synergistic effects may offer additional advantages of being multifunctional. Recent developments in experimental methods and computational techniques, such as density-functional theory (DFT) and molecular dynamic methods, provide new tools for designing and synthesizing tailored molecules with unique properties.

## CO<sub>2</sub> SORBENTS

Sorbents are used to remove CO<sub>2</sub> from a gas stream typically at higher temperatures than those used for absorbents, up to 700 °C or 800 °C in a combustion process. The common sorbents are metal oxides, such as calcium oxide (CaO). These materials chemically react with the carbon dioxide, in the case of CaO by forming carbonates. In most cases, the sorption capacity is limited to about 30 percent—that is, only about 30 percent of the CaO is converted to carbonate. The capacity can be improved by better engineering of the pore structure of the CaO in which case close to 100 percent capacity can be achieved. However, significant improvements in the operational characteristics of the sorbent would make this approach much more attractive. A desirable sorbent should have high CO<sub>2</sub> capacity (up to 100 percent of theoretical capacity), function in the presence of water vapor in the gas stream, and have fast reaction and regeneration kinetics, high durability, and the ability to be regenerated with minimal energy consumption. Sorbents that can operate at high temperatures (600 °C to 700 °C) could eliminate the need to cool the gas. The ability to remove other pollutants also is desirable.

High-temperature sorbents can also be applied to the production of hydrogen from fossil fuels. Natural gas or coal can be gasified to a mixture of carbon monoxide and hydrogen (CO/H<sub>2</sub>). Increased hydrogen production is traditionally achieved by employing the water-gas shift (WGS) reaction. However, the equilibrium of the WGS reaction requires a low reaction temperature in order to achieve high hydrogen concentration. Research is under way to separate hydrogen from high-temperature gas mixtures by means of high-temperature hydrogen separation membranes to shift the equilibrium toward hydrogen formation. Similar results can be achieved by removing CO<sub>2</sub> from a high-temperature gas mixture by the reaction of CO<sub>2</sub> with high-temperature sorbents, leading to the production of pure hydrogen. Metal oxides can also be effective for multifunctional pollution control. For example, calcium-based sorbents can react with sulfur oxides, hydrogen sulfide, and chlorine to a high extent as well, thus reducing their concentration in effluent streams to parts per million (ppm) levels.

New oxide compositions (e.g., multicomponent oxides, supported oxides) and/or oxides of engineered porosity are candidate materials. Completely novel sorbents, such as a

solid sorbent that becomes a liquid, or a liquid that turns into a solid upon adsorption of CO<sub>2</sub>, may offer significant advantages. Using modern computational methods and experimental techniques developed for the design and synthesis of nanostructured materials, it may be possible to engineer materials with tailored pore structures and connectivity, particle size, and chemical environment of the binding sites. Research and development on such materials can lead to breakthrough discoveries in adsorption technology.

### NANOSCALE MATERIALS AS SEPARATION AGENTS

Nanotechnology offers the potential to make materials with nanometer-sized dimensions. It also allows the predictable fabrication of structures with similar dimensionality. The appeal of these materials and structures is that they can have physical and chemical properties different from those of their larger-scale counterparts.

The potential of these nanoscale materials in separations technology is just beginning to be demonstrated. Separations technology is based on the physical and chemical interactions between the separations agent and the molecules that need to be separated. Physical properties such as pore size dimensions, pore size distribution, and connectivity have a major impact on the effectiveness of the separations agent. The chemical interactions between the separations agent and the molecules to be separated are also of paramount importance. These can be dramatically different at the nanoscale. Functionalization at the nanoscale may also prove to be more effective in terms of selectivity toward small molecules as well as the ability to change the binding energy.

Nanoscale porous structures in which molecular exclusion is the basis for many concepts in membrane separations offer the potential for greater selectivity. Nanoscale porous structures with minimum irregularities in the molecular path may significantly increase the molecular flux through the pores. This is a very important feature, since a major barrier to the use of membranes in large-scale separations is inadequate flux through membranes. Methods to design and construct such structures and their incorporation into defect-free membranes are research opportunities.

### HIGH-TEMPERATURE MEMBRANES

There is a need for novel membranes that can perform the separation of CO<sub>2</sub> and H<sub>2</sub> at high temperature (700 °C to 800 °C) and pressures above 20 bars. These membranes must show very high permeation rates in order to be an option for the large-scale separation of hydrogen and CO<sub>2</sub>. Moderate selectivities are sufficient in the case of CO<sub>2</sub>. High selectivities are required for hydrogen.

Membrane types under development include polymeric materials, microporous membranes, and liquid membranes, as well as solid membranes. For the needs described, solid membranes offer the greatest potential. Significant progress has been made in the development of ionic membranes for use in solid oxide fuel cells and for the high-temperature separation of oxygen from air. Novel concepts that build on these developments are needed for the effective separation of hydrogen and CO<sub>2</sub> at high pressures and temperatures. Nanoscale membranes that are thermally and mechanically stable and that do not require a support or that can utilize a support that is not flux-limited will represent a major technology breakthrough.



Another promising area of research is in the design of high-temperature, stable porous structures that have the porous space filled with functionalized molten salts. The molten salts would perform the separation, taking advantage of facilitated transport mechanisms since the molten salts need to operate under minimum pressure differential. These structures will require stable, nonvolatile molten salts with high permeance and good selectivity.

### ELECTROCHEMICAL APPROACHES FOR GAS SEPARATIONS

Most state-of-the-art gas separation technologies require significant expenditures of energy. For example, adsorption and desorption processes require energy to regenerate the separation agent. In other separations that are driven by pressure differentials, the separated product stream is at low pressure. Since in most CO<sub>2</sub> sequestration schemes it is necessary to produce high-pressure CO<sub>2</sub>, many separation schemes require expensive and energy-intensive compression of the CO<sub>2</sub>.

Electrochemical approaches that allow the recovery of CO<sub>2</sub>, hydrogen, and other gases from low-pressure streams deserve more attention. Conceptually, one can envision absorbing the low-pressure gas and pumping the gas-rich absorbent to high pressure. Pressurizing a liquid requires only a fraction of the electrical energy required to pressurize a gas. The challenge is to desorb the gas at this high pressure and regenerate the absorbent. Electrochemical methods could be a novel way to accomplish this desired step.

It is known that electrolysis of water can result in high-pressure hydrogen and oxygen. Experiments have been reported in the literature indicating that CO<sub>2</sub> can be absorbed in the liquid at pressures below atmospheric and desorbed at atmospheric pressure in an electrochemical redox system.

Research that leads to absorbents that have a high capacity for low-pressure CO<sub>2</sub> and whose CO<sub>2</sub> solubility at high pressure can be controlled using electrochemistry offers significant promise. Systems that incorporate redox agents that have different binding strength for CO<sub>2</sub> depending on the oxidation state are also promising.

### SMALL-SCALE WIDELY DISTRIBUTED CO<sub>2</sub> RECOVERY PROCESSES

Significant potential impact on the management of greenhouse carbon would result if economic processes were developed to recover CO<sub>2</sub> from distributed sources, such as exhaust gases from transportation vehicles, or from dilute sources such as the atmosphere.

Although the weight of the absorbent and the absorbed CO<sub>2</sub> together is many times the weight of fuel burned, onboard absorption systems suitable and selective for extracting CO<sub>2</sub> from exhaust gas should be considered. CO<sub>2</sub>-saturated absorbers might be exchanged for fresh ones at the time of refueling. An infrastructure could be developed to collect and centrally process the absorbers for sequestration and regeneration.

Similarly, passive, home-scale, distributed absorption systems might be developed for CO<sub>2</sub> removal from the atmosphere. Suitable distributed passive systems—based on bodies of water, absorbers, adsorbent materials, and biofiltration systems—deserve more attention. A centralized collection infrastructure capable of regenerating distributed absorbents may be required.

New families of absorbents (or adsorbents or membranes) will need to be developed for use with systems to recover CO<sub>2</sub> directly from the atmosphere. Such absorbents will need

to be more effective than today's amines at the 400- to 500-ppm CO<sub>2</sub> concentration range, but they will have to be less costly to regenerate than hydroxides. It may be necessary to extend or develop new structure-property relationships from existing or new experimental data to identify new molecular compositions and materials.

Finally, it may be possible to develop distributed systems to recover CO<sub>2</sub> from small domestic point sources or even from the atmosphere to produce materials such as fuel-grade methanol at rates significantly greater than cultivating biomass for use as a fuel feedstock. Such systems may be driven by photochemistry, electrochemistry, or diurnal temperature swings. (See the discussion in [Chapter 5](#), "Novel Niches.")

In all cases, novel passive absorption materials and systems as well as low-cost (capital and energy) regeneration systems need to be developed.

### CARBON MANAGEMENT THROUGH CARBON MONOXIDE

In the gasification of fossil fuels, most of the carbon is in the form of carbon monoxide. The conventional processing options for this gas are combustion to CO<sub>2</sub> (for electric power or heat generation), reaction with water to produce hydrogen and CO<sub>2</sub>, or reaction with hydrogen to produce a broad range of chemical and fuel products. In a scenario in which carbon management (collection and sequestration) is desired, it is worthwhile to explore ways to achieve this through use of carbon monoxide.

One starting venue would be the production of power by means of a partial combustion process designed to produce carbon monoxide as the principal product. The energy or power from the partial combustion will be less than it would be if the fuel were fully combusted to CO<sub>2</sub>. However, carbon monoxide may be easier to capture, separate, and "store" than CO<sub>2</sub>. Moreover, carbon monoxide can be more easily converted to useful products than CO<sub>2</sub>. It is important to keep in mind that all of these reaction schemes require hydrogen. If the hydrogen is derived from fossil fuels using conventional technology, this option is not attractive. Thus, it is essential that novel ways to produce this hydrogen be part of the equation.

In the case of this carbon management option, the first step should be an engineering evaluation of novel process concepts that encompass the whole carbon cycle, starting from the fossil fuel and including the separation, transportation, and sequestration of the ultimate carbon species. Simple energy and material balances can help identify attractive options that can guide the selection of novel materials and process chemistry concepts. These schemes should include process concepts in which heat and/or electric power is generated while the carbon monoxide is converted to an easily "sequestrable" state. It should also include concepts in which carbon monoxide is converted to fuels and chemicals as an intermediate step leading to simpler recovery and sequestration of carbon.

### NOVEL HYDROGEN STORAGE CONCEPTS

The production of hydrogen by means of gasification of coal (or other low-quality carbonaceous feedstocks) offers a low-cost route to fossil fuel decarbonization. With current technology, hydrogen (gas) can be produced from coal in large plants with near-zero emissions of carbon dioxide at costs in the range of \$1 to \$1.75 per kilogram (equivalent to

\$1 to \$1.75 per gallon of gasoline equivalent).<sup>1,2</sup> But the real cost of hydrogen to automotive consumers can be 2 1/2 to 3 times as much. The high retail cost of hydrogen inhibits the development of a hydrogen economy.<sup>3</sup> The large difference between the retail and wholesale costs of hydrogen arises in large part because the volumetric energy density of hydrogen is low (with gaseous hydrogen at 350 bar, one-tenth that of gasoline). The only commercially viable strategy for hydrogen storage in a vehicle at the present time is compressed gaseous storage (350 to 700 bar), which is costly not only for the storage canisters onboard vehicles but also for the compressors and electricity required for compression at refueling stations. Refueling time and safe hydrogen storage and handling facilities at retail stations are also factors that have a negative impact on the development of a hydrogen economy for transportation.

A low-cost hydrogen storage technology offering high volumetric storage densities with modest pressurization requirements could lead to a major reduction of the retail-wholesale gap for hydrogen. A mid-sized car with a hydrogen fuel cell could have a fuel consumption of 1 kg of hydrogen per 80 miles (80 miles per gallon of gasoline equivalent). If the desired range is 350 miles, a storage system with 4 percent hydrogen by weight translates to less than 120 kg of total weight. This weight penalty can be offset by reductions in the weight of other auto body parts.

Some present hydrogen storage sorbents have capacities below the target indicated, other sorbents suffer deterioration in use, and still others require complex systems to handle the energy requirements during sorption and desorption.

However, the range of materials investigated until now has been limited (metal hydrides, carbon). The theoretical design of sorbents (liquids or solids) with unique compositions and structure coupled with favorable physical and chemical interactions with hydrogen molecules is a good starting point for further research.

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<sup>1</sup> Williams R.H. Decarbonized Fossil Energy Carriers and Their Technological Competitors. Prepared for the International Panel on Climate Change Workshop on Carbon Capture and Storage, Regina, Saskatchewan, Canada, 18–21 November 2002.

<sup>2</sup> Simbeck D.R. and Chang E. Hydrogen Supply: Cost Estimate for Hydrogen Pathways—Scoping Analysis. NREL/SR-540–32525. July, 2002. Golden, CO: National Renewable Energy Lab.

<sup>3</sup> The hydrogen economy has been envisioned as the large-scale use of hydrogen as an energy carrier generated from any of a variety of fuels or feedstocks, to be used in the transportation, industrial, and building sectors, and requiring an infrastructure for its transmission and delivery.

### 3

## Advanced Subsurface Technologies

To date, deep, long-term subsurface storage of CO<sub>2</sub> has been demonstrated in conventional reservoir formation rocks (e.g., in depleted reservoirs). The workshop sessions on advanced subsurface technologies sought to broaden the menu of options beyond demonstrated techniques and identify novel ways to manage carbon utilizing the properties of the subsurface environment. The unique characteristics of deep environments can potentially be exploited for the following purposes:

- To store liquid CO<sub>2</sub> under pressure with surety (in some cases as a liquid),
- To effect “permanent” chemical or biological subsurface sequestration of CO<sub>2</sub>,
- To convert CO<sub>2</sub> to useful products, and
- To ensure environmental security.

The discussion during the sessions accordingly focused on the following questions and challenges:

- Where do such environments exist?
- What engineering means could be employed to create or access such environments?
- What technologies would need to be developed to achieve exploitation?

The subgroup discussed many potential areas of research and selected ideas in the following categories:

- Unconventional CO<sub>2</sub> storage formations;
- Increased use of CO<sub>2</sub> in enhanced oil recovery;
- Microbial hydrogen generation from fossil fuels at depth, with subsurface fuel cell coupling; and
- Deep-sea contained storage.

### UNCONVENTIONAL CO<sub>2</sub> STORAGE FORMATIONS

Deep, long-term underground storage of CO<sub>2</sub> is being conducted today in various parts of the world in depleted reservoirs. The formations at these reservoirs essentially represent conventional reservoir formation rocks that have been well studied. To meet the potentially dramatic increase in demand for storage of CO<sub>2</sub> in areas that may not have conventional storage formations available, unconventional formations must be explored as alternatives to the costly transport of CO<sub>2</sub> over very long distances.

Concepts of operation that may be used to stimulate thinking about this type of storage include the injection of CO<sub>2</sub> into formations with particularly favorable containment properties. When injected into sandstone formations derived from basalt at depths of about 2 km, CO<sub>2</sub> is expected to react with the chemical composition of the basalt and to form

carbonate precipitates, fixing the CO<sub>2</sub> at depth. Studies on the global availability and capacity of such formations overlain with competent, impermeable formations will be required. Modeling and experiments on CO<sub>2</sub> interactions with basalt should point to the level of benefit that could be derived from exploiting these formations for storage.

CO<sub>2</sub> could potentially be injected into deep (greater than roughly 3 km) ocean sediments at depths where the pressure/temperature regime will result in a stabilized CO<sub>2</sub> with a density greater than that of water. This would essentially isolate the CO<sub>2</sub> from seawater to inhibit chemical interactions. Studies of the global availability of such environments and of their porosity, permeability, and capacity would be of specific interest.

CO<sub>2</sub> could also potentially be injected into subsea tectonic spreading regions, which are highly active geothermally, creating unique geohydrologic activity. Seawater flows downward into the sediment at distances of many meters to kilometers away from the spreading area, then turns toward the region at depth and is eventually heated to high temperatures and expelled back to the sea. The conditions surrounding these regions have many advantages for fixing CO<sub>2</sub> in that the reaction kinetics are fast because of increasing heat and pressure in the direction of flow. It is theorized that CO<sub>2</sub> could be injected into the geohydrologic flow field away from the spreading region and entrained in that flow. This would result in the development of several carbonate species (magnesite, magnesium carbonate, dolomite, and calcite) as the combined flow of seawater and CO<sub>2</sub> is heated, pressurized, and released back to the sea.

Another possibility is Arctic hydrate storage of CO<sub>2</sub> below the permafrost layers in regions where methane and other gas hydrates form. The injected CO<sub>2</sub> would form CO<sub>2</sub> hydrates that would reside in the pore space of the host rock, with the permafrost layer above it serving, in effect, as the cap rock of a newly created CO<sub>2</sub> reservoir.

### Research Areas

Opportunities may exist in unconventional storage formations for utilizing the chemistry, temperature, and pressure (depth) to improve the long-term stability of sequestered CO<sub>2</sub> through mineralization, precipitation, and other stabilizing reactions.

Possible research concepts include the following:

- Characterization of promising, previously unstudied porous rock mass formations from a storage media perspective. This investigation would include examining porosity, permeability, capacity, and chemical composition.
- Identification of regional and global locations of favorable formations.
- Investigation, through modeling and experimental work, of the nature of rock/CO<sub>2</sub> fluid interactions in various rock types over short and long periods. The goal would be to determine beneficial interactions that may occur in basalt or sandstones derived from basalt.
- Assessment of containment issues such as interactions that may occur in surrounding and overlying rock types and performance of typical rock mass characterization.
- Accumulation and analysis of existing data on CO<sub>2</sub> storage. This activity should include examination of natural storage areas as well as engineered storage areas.

Specifically, experiences with injection and fate of CO<sub>2</sub> in enhanced oil recovery should be studied.

- Examination of the characteristics of geologic formations that now hold and have held CO<sub>2</sub> over geologically significant time scales.

### **INCREASED USE OF CO<sub>2</sub> IN ENHANCED OIL RECOVERY**

Some tens of millions of tons of CO<sub>2</sub> are currently used for enhanced oil recovery (EOR), but CO<sub>2</sub> is not available in many oil fields where it could be used. A relatively concentrated CO<sub>2</sub> stream can be generated in integrated gasification combined cycle (IGCC) coal-burning power plants. An economic synergy might be achieved if new IGCC plants could be located near oil fields that could use the concentrated CO<sub>2</sub> output. Additionally, regulations could be established to create incentives for the use of CO<sub>2</sub> in enhanced oil recovery and to discourage the use of naturally stored CO<sub>2</sub> in ways that ultimately vent it to the surface.

#### **Research Areas**

The current practice of using enhanced oil recovery indicates that CO<sub>2</sub> disposal could be applied almost immediately. This process would result in immediate incremental increases in CO<sub>2</sub> sequestration, provided that CO<sub>2</sub> from energy-producing plants can be efficiently delivered to the oil fields. Oil reservoirs could be simultaneously filled with CO<sub>2</sub> in a long-term storage scenario as oil is removed from the reservoir. This would avoid the near-certain loss of valuable storage space when the oil reservoir is completely depleted before it is ever reengaged to serve as a storage medium.

Possible research concepts include the following:

- Identifying economical means of transporting CO<sub>2</sub> from energy-producing plants to the oil fields and quantifying costs in rough orders of magnitude;
- Identifying additional infrastructure requirements and costs to employ EOR on many more reservoirs than those that current practice uses;
- Identifying the potential for CO<sub>2</sub> consumption through EOR if EOR were used in various percentages of all oil production worldwide; and
- Considering credit and penalty schemes to create incentives for using CO<sub>2</sub> for this purpose.

### **MICROBIAL HYDROGEN GENERATION FROM FOSSIL FUELS AT DEPTH, WITH SUBSURFACE FUEL CELL COUPLING**

The objective of microbial hydrogen generation from fossil fuels at depth, with subsurface fuel cell coupling, is to use microorganisms to degrade fossil fuels and couple the generation of hydrogen from this process with a fuel cell or other device to capture energy and prevent the formation of CO<sub>2</sub>. It has been known for several decades that certain microorganisms under anaerobic conditions degrade hydrocarbons. For one microbial degradation scenario, the process is inhibited by low concentrations of H<sub>2</sub>, which is a product of the microbial hydrocarbon degradation. The premise of this technology concept is to



harvest the low concentrations of aqueous  $H_2$  using a novel fuel cell or to apply other novel technologies to obtain energy from this microbial degradation without generation of  $CO_2$ . Microorganisms of the family *Geobacteriaceae* have been shown to oxidize a variety of aromatic hydrocarbons with the reduction of Fe(III). When Fe(III) was replaced with a graphite electrode as the electron acceptor, current production with organic oxidation was achieved.<sup>1</sup> It may be possible to harvest energy from the hydrocarbon oxidation using an electrode configuration.

In situ application of this technology would be highly desirable from an environmental standpoint, because energy generation would occur in the subsurface, minimizing the environmental impacts of mining the fossil fuel, bringing the material to the surface, and processing it at existing power plants. Also, no  $CO_2$  would be produced during the energy generation process using the proposed microbial technology. If such a process could be effectively developed, it could play an important role in limiting  $CO_2$  levels in the atmosphere.

### Research Areas

Because of the novelty of this process, considerable basic research and substantial process development are required as well as new energy-capturing technologies. Engineering design and pilot testing of the proposed microbial technology are likely only with major breakthroughs in microbiology as well as in energy-capturing technology.

Major research needs include the following:

- Identification and culture of microorganisms capable of rapid fossil fuel degradation;
- Optimization of conditions for rapid fossil fuel biodegradation to enhance the kinetics of the reactions;
- Optimization of technology to rubbilize coal in the subsurface, maximizing surface areas for reactions; and
- Development of a fuel cell or an electron-accepting device capable of effectively harvesting extremely low concentrations of  $H_2$  or other forms of energy from aqueous solutions.

### DEEP-SEA CONTAINED STORAGE

The idea behind deep-sea contained storage (DSCS) is that  $CO_2$  is piped under pressure to a depth greater than about 3000 m in the ocean, a depth at which the  $CO_2$  is a liquid that is denser than seawater. The  $CO_2$  is then stored in very large containers on the ocean floor. The first concept for a storage container is a 100-m diameter bladder, perhaps 1 km long. The container could be compartmentalized to minimize  $CO_2$  release in the event of container failure. Other containment options could be considered.

<sup>1</sup> Bond D.R., Holmes D.E., Tender L.M., and Lovley D.R.. Electrode-Reducing Microorganisms that Harvest Energy from Marine Sediments. *Science* 295:483, 2002.

Deep-sea contained storage of CO<sub>2</sub> may also make H<sub>2</sub> production from methane clathrates more attractive economically and environmentally. One of several issues surrounding the harvesting of methane clathrates for H<sub>2</sub> has been the question of what to do with the CO<sub>2</sub>. DSCS may offer a solution. A seafloor manufacturing facility could be constructed for methane clathrate processing. The CO<sub>2</sub> from this processing facility could be pumped directly to nearby CO<sub>2</sub> deep-sea storage containers.

Following are some key arguments that point to the importance of DSCS:

- Capacity could be expanded indefinitely. Some 125 containers, as described above, would store 1 km<sup>3</sup> or 1 Gt of CO<sub>2</sub>.
- CO<sub>2</sub> could be recovered, if desirable, or transferred to another container, if there was danger of leakage.
- Ordinary leakages would be comparatively benign.
- First estimates of infrastructure development, costs, and time appear to be far less than estimates for sequestering CO<sub>2</sub> in traditional subsurface storage formations, given that the volume of CO<sub>2</sub> that needs to be sequestered is equal to or greater than the total production capacity of the global petroleum industry. Thus, if used exclusively to meet storage requirements, conventional subsurface storage would require essentially duplicating the existing worldwide petroleum production infrastructure.
- There is precedence for this type of storage, as fuel is already stored in large containers in the sea. A considerable body of knowledge and technology already exists for this type of ocean storage.

### Research Areas

At this early stage in concept development, operational concepts are needed that consider types of bladders or other containers, their manufacture, deployment, filling, CO<sub>2</sub> diffusivity, and longevity. Concepts must include rough order-of-magnitude engineering cost estimates. Ocean floor pipeline considerations must also be included.

Major research areas include the following:

- The cost of compressing CO<sub>2</sub> and pumping it to the deep-sea bed for disposal in the containers;
- Environmental issues;
- Security issues—the total seabed area that would be required to sequester approximately 1 Gt of CO<sub>2</sub> for this type of disposal is not large (estimated at 5 km × 5 km × 100 m deep) in comparison with deep-sea disposal without containment; limiting the disposal area would enable better surveillance of the area; and
- Container protection—the container could be engineered so that it is encapsulated with stronger materials (e.g., cement) to afford it greater protection.



## 4

### Advanced Geochemical Methods for Sequestering Carbon

Emissions of CO<sub>2</sub> from the use of fossil energy may be controlled by capturing CO<sub>2</sub> in energy production facilities and then injecting the CO<sub>2</sub> into deep sedimentary formations. The capture and storage of CO<sub>2</sub> poses two principal difficulties: (1) the capture of CO<sub>2</sub> from combustion products is energy-intensive, expensive, and likely applicable only to large-scale stationary processes; and (2) the buoyancy of gas-phase CO<sub>2</sub> in reservoirs poses inherent risks of leakage.

In contrast, CO<sub>2</sub> is naturally captured directly from the atmosphere by its reaction with silicate minerals to form carbonates as rocks are weathered. Unfortunately, this process, while thermodynamically favored, is very slow. If such weathering processes could be artificially accelerated, it might be possible to manage the CO<sub>2</sub> produced by fossil fuels while avoiding some of the difficulties of conventional CO<sub>2</sub> capture and storage. Geochemical immobilization can effectively eliminate the risk of CO<sub>2</sub> leakage. In addition, the use of geochemical processes allows the direct capture of CO<sub>2</sub> from the air, thus potentially lowering the cost of managing emissions from dispersed sources.

Research is needed in the following broad areas:

- Assessment of the reactivity, abundance, and economic availability of suitable alkaline minerals and rocks;
- Development of processes that can accelerate the carbonation reactions; and
- Assessment of the capacity, cost, and environmental impact of these processes.

#### CHEMICALLY ENHANCED WEATHERING

It has been found that the rate of the very slow natural carbonation reactions of magnesium silicate minerals can be greatly accelerated by high-temperature pretreatment. Reduction to ultrafine particle sizes also helps. Both of these options are energy-intensive, however, and probably not practical. The minerals react readily with mineral acids, but the resulting salts no longer can react with CO<sub>2</sub>. It may be possible, however, to find reagents that can convert only a small portion of the rock, so as to leave a porous structure, which can then react with CO<sub>2</sub>.

#### Research Areas

Research is needed on chemical methods to accelerate the natural weathering process by which minerals form carbonates.

Following are specific questions that need to be addressed:

- Could low-cost chemical methods be used to “pretreat” silicate minerals in order to facilitate the removal of metal ions and speed up the carbonation reactions?

- Can chemistry help maintain carbonates in solution so they do not immediately precipitate on surfaces, which slow or stop subsequent carbonation reactions?

### **BIOLOGICALLY MEDIATED ENHANCEMENT OF WEATHERING PROCESSES**

Biological processes might be used to accelerate the weathering process. This acceleration might, for example, be implemented in large leaching piles such as those used for biologically mediated extraction of copper from ores. Microbes may be able to enhance the physical weathering of magnesium (Mg)- and calcium (Ca)-containing silicate minerals, as well as to enhance the liberation of the metal ions from their mineral form. Strong acids could be used to achieve this same goal, but in this case large amounts of acid would be required to liberate significant quantities of the metal ions, energy would need to be added to recover the acid, and the carbonation reaction would no longer be spontaneous.

Microbiological systems may be able to circumvent these limitations by selectively producing acid in quantities large enough only to break up the minerals while providing an important mechanism to enhance metal extraction. In this context, biological processes would not leach the bulk of the alkaline source rock but would be used to mechanically decompose rock particles, increasing surface area and thereby increasing the rate at which subsequent processing could dissolve rock and make carbonates.

Biological systems can play an important role in significantly enhancing the natural rate of weathering, which occurs on extremely long time scales (approximately  $10^5$  to  $10^6$  years). They could speed up these processes by breaking up mineral particles and increasing the reactive surface area. This is possible if the microbes or bacteria act very specifically (for example, producing acid) in key locations to help break apart the mineral structure. These bacteria could further speed the process by increasing the liberation of metal ions from the silicate minerals. Producing a carbonate mineral could be achieved by then combining these systems with some form of  $\text{CO}_2$  (such as aqueous, supercritical, or gaseous).

A key consideration with respect to the use of biological systems to enhance the rate of weathering is the potential leverage available to the microbes. Because of the large quantities of silicate minerals necessary to sequester industrially interesting quantities of  $\text{CO}_2$ , it is crucial that each microbe be able to help liberate several orders of magnitude more metal ions than the amount of acid produced.

### **Research Areas**

The aim of research will be to identify the role that bacteria and microbes can play in enhancing the weathering process of serpentine (or similar) minerals to extract suitable metal ions ( $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ) to neutralize carbonic acid. It will be necessary to understand the scale, biochemistry, and kinetics of each of these processes and reactions.

Following are some specific questions that need to be addressed:

- Can biological systems extract energy from the overall exothermic and spontaneous carbonation reaction? Are other energy sources and nutrients required for the microbes?

- What are the mechanics by which bacteria and microbes could influence the weathering of silicate minerals? Do they tend to help break up larger mineral structures?
- In nitrogen-containing minerals, can nitrifying bacteria cause weathering?
- What is the potential increase in reactivity of the weathered rock?
- Are there biological mechanisms for extracting and/or liberating free or complexed metal ions from the silicate (i.e., serpentine) minerals?

### MICROBIAL FIXATION OF CO<sub>2</sub> TO FORM CARBONATE MINERALS

Cyanobacteria are known to use their photosynthetic energy to generate small quantities of calcium carbonate (CaCO<sub>3</sub>). In the Green Lake in Fayetteville, New York, species of synecococcus have been shown to deposit significant amounts of CaCO<sub>3</sub> at the bottom of the lake in summer months. As noted, silicate minerals could be utilized as the source of Mg<sup>2+</sup> or Ca<sup>2+</sup> ions. It is not known whether any microbes are able to utilize Mg<sup>2+</sup> to form magnesium carbonate (MgCO<sub>3</sub>). Selective techniques could be used for developing cyanobacterial strains that will be able to effectively utilize free Mg<sup>2+</sup> ions to form MgCO<sub>3</sub>.

The carbonate formation ability of biological systems is not well understood. Further understanding of this process can help enhance the carbonation reaction once a suitable source of alkalinity is present. Microbial carbonate formation can be coupled to biologically mediated metal ion extraction from silicate minerals to provide one possible pathway for CO<sub>2</sub> immobilization. Potential benefits to microbial carbonation reactions include increasing carbonation reaction rates as well as increasing the presence of chemical factors that could help solubilize the carbonate after formation, so that the microbes can keep the surface of the silicate minerals free for further weathering reactions. These reactions could be carried out in industrial-scale bioreactors, large leaching piles, or in situ underground.

#### Research Areas

Research is needed to understand the biochemistry and regulatory aspects involved in the carbonation reaction in bacteria and microbes and how it might help us increase the rate and/or lower the cost of forming magnesium carbonates.

Following are specific questions that need to be addressed:

- What is the role of CaCO<sub>3</sub> formation in microbes?
- Can cyanobacteria that can utilize Mg<sup>2+</sup> to form MgCO<sub>3</sub> be found, isolated, and engineered?
- What are the characteristics of the genes and enzymes involved in this process, and what are the factors that influence their regulation?
- What chemical means are utilized to keep carbonate minerals in solution to prevent blocking or inactivating the surface area with carbonates?
- What is known about side reactions?

## FORMATION OF IRON CARBONATES

There are various basic minerals containing iron in the +2 oxidation state that can react with CO<sub>2</sub> to form iron carbonate (FeCO<sub>3</sub>). Possible options include oxides, silicates, and perhaps sulfides. Compared to magnesium silicate minerals, these minerals have the disadvantage of being unstable relative to oxidation, since the +3 oxidation state does not form a stable carbonate. However, under specific conditions, they could provide an important energy source by means of redox reactions for bacteria, and may have different, possibly faster, weathering properties. Under the conditions in which they are typically encountered, they have been stable for millions of years.

The option of iron carbonation has not been studied nearly as extensively as that of magnesium carbonation, and further research needs to be performed to understand the advantages and disadvantages of these iron carbonation processes. Options for utilizing the base iron minerals are similar to those for magnesium bases except that oxygen must be avoided and a fairly narrow pH range is required for formation of the carbonate.

### Research Areas

Research is needed to understand the chemistry involved in the carbonation reaction in iron and microbes and how it might help increase the rate and/or lower the cost of forming iron carbonates.

Following are specific questions that need to be addressed:

- What conditions are required to enhance the thermodynamics and kinetics for forming stable iron carbonates?
- What role can reduced iron play in providing energy for bacteria to speed the weathering and carbonation reactions of iron- and non-iron-containing minerals?

## ENHANCED DISSOLUTION OF CO<sub>2</sub> IN BRINES

A major concern about the stability of supercritical CO<sub>2</sub> storage in deep aquifers relates to its buoyancy. Less dense than water, CO<sub>2</sub> will float under the top seal atop the water in an aquifer and could migrate upward if the top seal is not completely impermeable. The stability of sequestered CO<sub>2</sub> in saline aquifers is much more certain if the CO<sub>2</sub> is dissolved in the liquid or precipitates as a carbonate in the formation. Brines with dissolved CO<sub>2</sub> have a greater density than that of CO<sub>2</sub>-free brines, and this greater density significantly reduces CO<sub>2</sub> buoyancy and leakage problems from subsurface CO<sub>2</sub> disposal. Dissolution disposal would facilitate the selection of aquifers as disposal sites, since the requirement for an impermeable top seal could potentially be relaxed, thereby expanding the number of possible disposal reservoirs. Over very long time scales, the CO<sub>2</sub> injected into very large saline aquifers with enough capacity will eventually dissolve into the brine and pose significantly reduced risk of CO<sub>2</sub> release. As with natural weathering, the natural dissolution of CO<sub>2</sub> in brines is too slow to be a practical storage solution on the large scale necessary.

The capacity of the brine in an aquifer to dissolve CO<sub>2</sub> is much greater if the pH of the brine is at the high end of the naturally occurring range. Such brines also open up options for enhancing the dissolution rate. They may also enhance the formation of carbonate

minerals. If the pH of a brine is high enough, it may even be utilized as an absorbent for CO<sub>2</sub> that would be disposed of and needs no regeneration.

### Research Areas

Research is needed to understand the capacity issues, engineering approaches, and physical and chemical conditions for enhancing the dissolution of CO<sub>2</sub> in brines.

Possible system concepts and research areas include the following:

- Brine is pumped from an aquifer to the surface to mix with moderately high-pressure CO<sub>2</sub> and is reinjected at another point in the aquifer. The CO<sub>2</sub> is envisioned to dissolve either in the aquifer or on the way down in the reinjecting well. Less CO<sub>2</sub> pressure would be required than that needed for direct injection of the CO<sub>2</sub>.
- Supercritical CO<sub>2</sub> is pumped directly into an aquifer where the dissolution process is enhanced by means of an in situ contactor or other chemical or physical means.
- Regarding absorbent or adsorbent transport of CO<sub>2</sub> to brines—CO<sub>2</sub> could be carried into deep aquifers by means of a low-cost disposable or regenerable chemical adsorbent or absorbent. At depth, the CO<sub>2</sub> would be transferred to the brine. If regenerable, the CO<sub>2</sub>-lean carrier would be recovered back at the surface in a loop process.
- If the pH of the brine is sufficiently high, it may be possible to use the brine as a first-stage absorbent for low-partial-pressure CO<sub>2</sub> in a flue gas stream, either in a conventional low-pressure-drop contactor or in a novel high-residence-time contactor. Cleanup with a conventional absorbent may be required to recover residual CO<sub>2</sub>.
- The physical and chemical processes that could enhance dissolution of CO<sub>2</sub> into brines need to be identified. The conditions and the brine compositions that are best for dissolution and/or mineralization need to be discovered.
- Studies need to be performed on acid recovery and potential by-products.

### Soils

Natural weathering rates are limited by, among other factors, the exposed surface area of chemically reactive rock. Weathering reactions might be accelerated simply by adding suitable alkaline rocks in powdered form to agricultural soils. This treatment would be particularly applicable in acidic soils. Breakdown of the source rock might be accelerated by biological mechanisms and by the high partial pressure of CO<sub>2</sub> in soils. Once the alkaline rock is dissolved, the metal ions might either form carbonates that remained with the soil or leach from the soils with run-off. In the case of run-off, the net effect would be to add alkalinity to the ocean, thereby removing CO<sub>2</sub> from the atmosphere.

### Research Areas

Research is needed to understand and develop methods to treat soils to accelerate natural weathering reactions and other processes favorable to removal of CO<sub>2</sub> from the atmosphere.

Research is needed in the following areas:

- To assess the weathering rates of suitable alkaline minerals in soils. Such research should enable crude prediction of how weathering rates depend on the size and pretreatment of the base rock, on the kind of soil, and on the means of application of the alkaline minerals.
- To increase understanding of the fate of metal ions leached into soils.
- To assess the impacts of adding small amounts of base to soils.

## 5

# Novel Niches

### INTRODUCTION

The objective of the Novel Niches sessions at the workshop was to explore potentially practical niche technologies for CO<sub>2</sub> conversion to useful products (including moderate to large-scale production of plastics and fuels), for CO<sub>2</sub> removal and sequestration from flue gases, for its removal from the atmosphere and storage, and for noncarbon energy production processes other than “conventional” energy technologies such as nuclear, biomass, and various renewable energy technologies. Important opportunities may exist either for the development of a novel concept of sequestration or for ways of applying new science and technology from areas far removed from current CO<sub>2</sub> sequestration efforts. These opportunities may occur in CO<sub>2</sub> separation, CO<sub>2</sub> capture, CO<sub>2</sub> storage, CO<sub>2</sub> recycling, or CO<sub>2</sub> conversion into useful commercial products.

For the most part, the discussions in the Novel Niches sessions concentrated on novel concepts involving CO<sub>2</sub> recycling and CO<sub>2</sub> products as well as on new scientific and technological means to achieve these goals. Also, the notion of a “niche” opportunity was thought of as an area that might contribute to ameliorating at least a small part of the carbon management issue but would not necessarily be the major approach to managing or “solving” the carbon problem (i.e., not a “silver bullet”). Thus, if a particular niche application could address the carbon problem in some small degree, the application of several niche technologies could make a significant contribution.

One main thrust of discussion concerned the general area of biomass production and use. Ideas were put forth on a number of possible new ways to enhance CO<sub>2</sub> uptake from the atmosphere by manipulating plant genetics, enzymes, microbes, cyanogens, and catalytic pathways.

Another area of potential advancement is that of the design of advanced catalysts (using nanotechnology) to allow carbon sequestration on an accelerated, less energy-intensive basis by promoting various carbon-based chemical reactions. The potential for new CO<sub>2</sub> separation technologies involving absorption on advanced-technology activated fibers was proposed as a way to reduce the energy cost of CO<sub>2</sub> capture and regeneration. (Also see [Chapter 2](#), “Advanced Separations Techniques.”)

Finally, the Novel Niches subgroup noted that, although this is not a technology related to carbon management, more accurate measurements of carbon fluxes between terrestrial, oceanic, and atmospheric reservoirs would enable better understanding of the carbon cycle. Of particular merit would be a better understanding of the potential to optimize the percentage of energy and carbon capture of the total energy and carbon flux in the immediate vicinity of growing terrestrial and marine systems. An enhanced understanding of the carbon cycle would offer the potential for advances in carbon flux manipulation that would improve opportunities for terrestrial and marine carbon sequestration.

The wide-ranging discussions of the Novel Niches sessions were organized in four areas in which there appear to be opportunities for carbon management if breakthroughs, improved scientific understanding, and new technology applications are developed. The four



areas are (1) biomass management, (2) catalytic and/or photolytic CO<sub>2</sub> reduction, (3) biocatalysts for CO<sub>2</sub> binding and reduction, and (4) technology opportunities. The following sections describe the basic concepts, discuss their potential significance, and indicate areas in which research presents opportunities for breakthroughs.

### **BIOMASS MANAGEMENT**

Terrestrial sequestration of carbon by biomass production is an approach for sequestering significant amounts of CO<sub>2</sub>. Sequestration through biomass offers the opportunity for CO<sub>2</sub> to be recycled through fuel utilization or value-added products or for CO<sub>2</sub> to be directly sequestered. Although biomass production systems currently exist, advances in the utilization of biomass for sequestration could have a significant impact on the adoption of this technology, since biomass processes offer the prospect of obtaining a high-concentration CO<sub>2</sub> stream from the processing of the methane or higher-molecular-weight compounds. These feedstocks would arise from aerobic or anaerobic biodigestion of biomass, gasification of biomass with subsequent chemical processing, or extraction of oils or solids from biomass for direct use or subsequent chemical processing. The products that could result from biomass-based processes include useful fuels such as methane, liquid ketones for hydrogenation into transportation fuels, and novel cellulose sheets. In addition, biomass is a possible means of producing a condensed phase of CO<sub>2</sub> that could be sequestered directly in the ground leading to a net removal of carbon from the atmosphere. Suggestions of novel means of drastically reducing the capital cost of a biomass plant were presented.

This area of biomass management is of importance for the following reasons:

- Research directed at novel approaches for increasing biomass production, improving processing, and enhancing utilization and sequestration would make a significant contribution to enhancing this technology.
- Recent advances in modern biology, including advances in genomic sciences, provide new and promising approaches for enhancing biomass production, enhancing biomass processing, and producing novel products.

### **Research Opportunities**

Areas in which research presents opportunities for breakthroughs in biomass management include the following:

- There is the opportunity to capitalize on advances in genomic science to develop a basic understanding of the biology of plants, which could lead to the development of approaches that will have a significant impact on biomass production. Research would include studies of basic mechanisms of CO<sub>2</sub> fixation, manipulation of plant respiration, altering the way in which carbon is partitioned to different parts and structures of plants, and enhancement of nitrogen use efficiency.
- Improvements are needed in the processing of biomass into either fuel or products, including opportunities offered by genomics, innovations in low-cost fermentation processes, or other conversion methods (e.g., thermal-chemical



conversion). Particularly needed are improvements—specifically reductions—in the following:

- The capital cost and complexity of the equipment, particularly that arising from the need for biological isolation,
  - The life-cycle energy required to produce fuels or products,
  - The amount of non-raw-material inputs (e.g., nutrients), and
  - The fraction of carbon that is respired versus that converted to products.
- Biomass also offers the opportunity to sequester CO<sub>2</sub>. It is possible that novel approaches for innovative sequestration processes could be developed and integrated with these methods. In particular, major opportunities exist for using microbes for enhanced, low-cost cellulose production with polymeric materials as substitutes for petroleum-based plastics.

### CATALYTIC AND/OR PHOTOLYTIC REDUCTION OF CO<sub>2</sub>

The basic notion of catalytic and/or photolytic reduction of CO<sub>2</sub> is to use inorganic catalysis or photosynthetic processes, possibly including photoelectric effects, to directly reduce CO<sub>2</sub> and water to form fuels such as methane (which could be used as fuel for heating and/or transportation) or higher-value carbon compounds (e.g., methanol, ketones, aldehydes, and acids) in a process with low capital and operating costs. Direct sunlight is envisioned as the source of the energy for the CO<sub>2</sub> reduction. The CO<sub>2</sub> may be in concentrated form as a pressurized high-density fluid from capture and transport processes, or it may be highly dilute as in the atmosphere. In a virtually all-electric economy, many forms of direct manufacture of electricity including photovoltaic energy would have significant advantages and would significantly reduce the emissions of carbon dioxide. However, the photolytic reduction of carbon dioxide might still be used to make starting materials from carbon and to make carbon-based fuels to whatever extent they are used. Carbon-based fuels would have significant storage and transportation advantages over electricity.

The application of a large-scale, single-cell photosynthetic culture has new potential for CO<sub>2</sub> utilization through the body of research carried out in the last several decades. Single-cell culture processes could be improved by employing more effective reactor designs and advanced light-capturing technologies. The production of single-cell microorganisms for useful polymeric products offers potential for a new CO<sub>2</sub>-based utilization.

Successful research in this area is of importance for the following reasons:

- Present photovoltaic devices demonstrate solar energy collection efficiencies per unit of area that are greater than that of photosynthesis. It is recognized that this greater collection efficiency comes at the expense of a much greater capital cost. That may well need to become the focus of the research.
- Success would lead to a fuel or higher-value hydrocarbon that could be used instead of fossil-based hydrocarbons in transportation fuels or chemical feedstocks.
- The technical, environmental, and economic challenges of sequestration would be avoided.
- The production of a hydrocarbon fuel or higher-value hydrocarbon would enable the equivalent of storage and transportation of sunlight energy, which is otherwise

discontinuous and not necessarily available on an as-needed basis at a particular point of use.

### Research Opportunities

Areas in which research presents opportunities for breakthroughs in the catalytic and/or photolytic reduction of CO<sub>2</sub> include the following:

- Inorganic catalysis studies leading to the right combination of materials and surface interactions to accomplish CO<sub>2</sub> reduction while supplying the necessary energy input at the surface and not in the bulk phase, and application of nanotechnology surface construction techniques to achieve sufficient selectivity;
- Devices that have low capital cost that capture sunlight energy and simultaneously channel that energy only to the catalytic surface;
- Prevention of reoxidation of the produced hydrocarbon back to CO<sub>2</sub> in the presence of the coproduced oxygen; and
- Photosynthetic microbial fixation of CO<sub>2</sub> at the surface with production of hydrocarbons, followed by subsurface sequestration of waste biomass through nucleation of metal carbonates.

### BIOCATALYSTS FOR CO<sub>2</sub> BINDING AND REDUCTION

A wide variety of microorganisms and their enzymes perform diverse chemical reactions that can be used for the binding and reduction of CO<sub>2</sub> from the atmosphere. Two new scientific developments in this field offer the opportunity to dramatically enhance the binding and affinity for CO<sub>2</sub> and the rate of reduction of CO<sub>2</sub> into an array of useful biochemicals. First, a wide variety of extremophiles (i.e., microbes that can grow at either high pH or low pH, high temperature or low temperature, at high salt, or that catabolize unusual substances such as CO, or metal salts) have been discovered. These organisms produce “extremozymes” that are stable and active under harsh process conditions. Second, the advent of molecular biological tools enables the biotechnologist not only to clone and overexpress these proteins in industrial hosts but to utilize site-directed and random mutagenesis to dramatically enhance the affinity of CO<sub>2</sub> binding and the rate of its conversion into useful biochemicals. Furthermore, the newest technology that has emerged enables the custom design of a combined CO<sub>2</sub>-binding and CO<sub>2</sub>-reducing enzyme system using protein fusion technologies.

A more efficient and rapid conversion of atmospheric CO<sub>2</sub> into a variety of reduced biochemicals can enable the following:

- The utilization of these extremophile genes and enzymes in biomass systems or biofilter systems (e.g., immobilized microbe or enzyme bioreactors) to consume CO<sub>2</sub> from the atmosphere or smokestacks or flue gases;
- The production of plant polymers from CO<sub>2</sub> such as cellulose, starch, and polyesters for application to high-volume markets; and

- The production of a wide variety of higher-value biochemicals by microbial CO<sub>2</sub> reduction, including ethanol and other organic alcohols, amino acids, succinic acid and other organic acids, and other polyesters.

### Research Opportunities

Areas in which research presents opportunities for breakthroughs in biocatalysts for CO<sub>2</sub> binding and reduction include the following:

- Characterization of CO<sub>2</sub> binding and reducing enzymes and their genes from extremophiles;
- Enhancement of enzymatic CO<sub>2</sub> binding efficiency, CO<sub>2</sub> reduction rates, enzyme stability, and acceptor substrate range by protein engineering techniques;
- Design of customized CO<sub>2</sub> binding and reduction biocatalysts composed of multiple enzymes using protein fusion technologies; and
- Investigation of opportunities offered by genomics and proteomics to improve microbial processes.

### TECHNOLOGY OPPORTUNITIES

There are niche opportunities to diversify and improve major technologies for CO<sub>2</sub> management. These range from CO<sub>2</sub> separation methods to accelerating the rate of sequestration or conversion of CO<sub>2</sub> to other materials. Niche technologies will expand and strengthen the portfolio of methods currently under development and offer potential for substantially higher efficiencies in fossil fuel use. The discussions in the Novel Niches sessions identified research opportunities with significant potential that are described below. One area identified, engineering systems analysis for optimum CO<sub>2</sub> reduction or sequestration, is a crosscutting opportunity and is discussed in [Chapter 6](#), Crosscutting Issues.

### Research Opportunities

The following niche technologies do not easily fit in any of the previous categories but may offer potentially large reductions in CO<sub>2</sub> emissions:

- *Separating carbon and hydrogen from coal.* This approach covers processes and concepts to differentiate solid carbon from hydrogen while avoiding coal combustion. The hydrogen would be used as fuel while the carbon would be used to produce carbon-based building and structural materials—for example, to substitute for cement and steel. Separation could be accomplished by coking, for example. The separated carbon could then be used to produce high-tensile-strength material, such as carbon fiber beams for a steel substitute, or high-compression material formed into carbon bricks for building and structural construction.

- *“Zero” emission processing.* This technology complements the process developments occurring in DOE's Office of Fossil Energy Vision 21 Program by looking for new, closed-loop fuel production/ electricity production cycles that involve essentially no pollutant emissions.
- *Direct flue gas treatment.* This area is crucial for application to commercial fossil-fuel combustion processes. There are methods that should be explored, including flue gas biofiltration or advanced CO<sub>2</sub> hydrate formation. (Also see [Chapter 2](#), “Advanced Separations Techniques.”)
- *Removal of CO<sub>2</sub> from ambient air.* Alternative methods for low-cost, efficient removal of CO<sub>2</sub> from the air may be feasible using biofiltration combined with wind-induced airflow through the filter. This area merits exploration as an alternative to biomass production. (Also see [Chapter 2](#), “Advanced Separations Techniques.”)

## 6

### Crosscutting Issues

#### REQUEST FOR PROPOSAL STRUCTURE AND PROJECT MANAGEMENT

In the course of the workshop, each subgroup addressed various issues of overall program management. This chapter of the report summarizes those discussions.

Although the purpose of the expanded DOE/FE program is to elicit novel concepts for carbon management and to reach more widely into the scientific community, the initial number of awards will be small and the initial funding for each project will also be small. The labor required for a full proposal may deter some of the very people DOE/FE desires to attract because of the low probability of success and the small stakes. DOE/FE could utilize a preproposal process, which invites a short, 3- to 5-page submission, followed by a limited invitation for full proposals. This process would have two benefits: (1) DOE/FE would receive more proposals with less early work required from researchers; and (2) DOE/FE may identify productive collaborations among preproposers that would not otherwise happen. Within DOE, both the Office of Science and Office of Environmental Management have used a preproposal process successfully.

The committee expects that DOE/FE will receive a range of proposals varying from specific technologies to systems concepts to fairly narrow exploratory research questions. To put them on a somewhat level playing field, it was noted that the request for proposals (RFPs) could require each full proposal to include a simple energy and materials balance analysis. Such an analysis would demonstrate that the proposer understands the larger technological context into which the project fits, even if it addresses initially a narrow but critical research question. This analysis needs to demonstrate that the scale of carbon sequestration achieved is commensurate with the problem, that the thermodynamics are real, and that there is some consideration of cost. The committee recognizes that some of the people DOE/FE wants to attract might not have the capacity to undertake this analysis on their own. The RFP could suggest collaborations with engineering groups, or DOE/FE could relax the rigor of this requirement in the first round. It might also consider establishing an internal DOE/FE group that could help proposers with this analysis.

The committee is also concerned about the postaward management of the program. The encouragement of communication among the awardees and other performers in the carbon sequestration program will be critical. DOE/FE could consider the establishment of annual sequestration review meetings that include presentations from the novel concept awardees. This would foster broader awareness of the new work but also facilitate collaborations that will advance both the novel concepts and the nearer-term projects.

The committee also notes that as the early awards mature, additional support may be necessary before investigators transition to other parts of the carbon sequestration program. In particular, exploratory research projects may transition to larger, multidisciplinary efforts requiring larger amounts of funding.

## CROSCUTTING ANALYTICAL AND ENGINEERING ISSUES

A few subgroups identified crosscutting technical issues that were not carbon management ideas per se but rather engineering and analytical issues associated with long-term carbon storage. Three such issues are described below.

### Monitoring and Containment Technologies Following Subsurface CO<sub>2</sub> Sequestration

Once CO<sub>2</sub> is sequestered in the subsurface by some means, it will be necessary to monitor the sequestered CO<sub>2</sub> to determine whether leakage is occurring. By necessity, detection technologies must be low in both capital and operating costs, highly sensitive, and capable of monitoring large areas of Earth's surface. The latter capability is essential, because the sequestered CO<sub>2</sub> may be spread out over large areas of the subsurface.

Equally vital are technologies that will be able to heal leaks in the subsurface. Sequestration of CO<sub>2</sub> may take different forms, ranging from storage in saline aquifers and deep subsurface coal beds to deep-ocean disposal methodologies; therefore, technologies to seal leaks must be diverse and effective in a range of subsurface environments.

CO<sub>2</sub> is likely to be stored in a variety of forms, ranging from pressurized CO<sub>2</sub> in subsurface environments to immobile mineralized forms. In some storage scenarios, the liquefied CO<sub>2</sub> will seek cracks and fractures in the geologic formation, abandoned wells in depleted oil fields, wormholes in the deep-ocean sediment storage areas, or tears in such proposed storage methods as deep-sea bladders filled with CO<sub>2</sub>. Although catastrophic CO<sub>2</sub> release is unlikely in most storage schemes, slow leakage is likely. These slow leaks not only must be identified but also must be effectively repaired to ensure secure storage of the carbon for long periods of time.

### Technology Opportunities

Monitoring technology must be capable of detecting CO<sub>2</sub> leaks through the existing atmosphere, on the terrestrial surface, on the ocean surface, and in the deep ocean. Technology concepts for monitoring could include such things as "tagging" the stored CO<sub>2</sub> with an odorant such as hydrogen sulfide (H<sub>2</sub>S) or a mercaptan that could be detected by gas analyzers, radioactive isotopes that could be traced, or spectrally detected compounds such as sulfur hexafluoride (SF<sub>6</sub>). Hyperspectral satellite imagery or change-conditions technology in a global monitoring context may offer technical opportunities for monitoring. For deep-ocean disposal, such as in a pressurized bladder that resides on the deep-ocean floor, an array of pH meters to monitor changes in ocean water pH may be sufficient.

Highly effective sealing technologies that can be employed remotely in the deep subsurface environment or the deep ocean must be identified and engineered. Opportunities may exist in technological extensions to conventional grouting methods, new polymer sealants may be developed, or biofilms and other biological methods may be developed for selectively sealing leaks. Promising technological developments need to be tested for effectiveness as engineered barriers to CO<sub>2</sub> mobilization.

### **Subsurface Technologies: Risk Assessment**

In the workshop discussions, it was suggested that DOE/FE request that each group or person submitting a proposal include a very introductory risk-benefit analysis of their research idea. This would then serve as the very beginning of a risk assessment for the concept. The preliminary risk assessment would provide context for considering the benefits of a carbon sequestration method.

Risk assessment, also known as total system performance assessment, could be utilized to estimate quantitatively the success of a subsurface carbon sequestration method. Risk assessments are based on conceptual models, which incorporate features, events, and processes that individually or in concert are judged capable of disrupting the ability of a sequestration system to contain CO<sub>2</sub> (or other chemical form of sequestered carbon). Quantitative probabilities are assigned to the occurrence of various events (e.g., seismic activity) and processes (groundwater flow), and estimates are made of the associated consequence—the amount of CO<sub>2</sub> released. Risk assessment can be used as a tool to develop a CO<sub>2</sub> release standard—that is, a level of CO<sub>2</sub> release that is judged safe and acceptable, taking into account distances from human populations and fate and transport of CO<sub>2</sub>, among other factors.

Risk assessment of subsurface CO<sub>2</sub> containment systems can leverage the existing capability of risk assessment of underground disposal (e.g., of nuclear waste), so cost for the risk assessment is not likely to be a barrier. Implementation could be accomplished swiftly, and information could be made available to decision makers about the suite of subsurface carbon sequestration methods.

### **Research Opportunities**

Research opportunities in the area of risk assessment are as follows:

- Development of conceptual models and inventories of features, events, and processes;
- Application of risk assessment methods to candidate sequestration ideas and candidate sequestration sites; and
- Development of an environmental CO<sub>2</sub> release standard.

### **Engineering Systems Analysis for Optimum CO<sub>2</sub> Reduction or Sequestration**

There is a major need for conceptual engineering analyses of novel process schemes as an adjunct to laboratory exploration of process elements. Early conceptual analysis for material and energy balance will provide for early screening of new technology concepts to ensure that fundamental physical laws have not been violated. These analyses would be specific to concepts developed for the niche technologies envisioned, as exploratory investigations advance.

Systems analysis, including preliminary cost analysis, would provide an opportunity to identify critical areas of accomplishment required for technical and/or economic success. While excessive use of such analysis can cripple innovation, its proper use can help identify and focus on the issues and needs that will ultimately affect success or failure.



### Research Opportunities

Research opportunities in the area of engineering systems analysis for optimum CO<sub>2</sub> reduction or sequestration would include developing basic information and methodologies to evaluate and compare the following:

1. Risk of human tragedy;
2. Potential for a major, abrupt reversal;
3. Magnitude of interaction with the environment;
4. Degree of the environmental unknowns;
5. Energy required per unit (per unit=per unit of CO<sub>2</sub> emission reduced);
6. CO<sub>2</sub> disposed/CO<sub>2</sub> processed;
7. Materials to be disposed of per unit;
8. Materials inputs required (e.g., nutrients) per unit;
9. Capital cost per unit;
10. Potential for continuous low-level leakage;
11. Physical footprint per unit;
12. Potential for remediation if/when a problem arises;
13. Operating cost per unit;
14. Potential for technology improvement;
15. Time required to commercialize; and
16. Total size of the opportunity.



## Appendix A

### Workshop Participants

#### LISTINGS BY SESSION

##### Plenary Session (speakers)

Martha A.Krebs,\* Science Strategies, *Session Chair*  
Scott D.Barnicki, Eastman Chemical Company  
Sally M.Benson, Lawrence Berkeley National Laboratory  
Charles Christopher, BP America, Inc.  
Scott M.Klara, National Energy Technology Laboratory, U.S. Department of Energy  
Michael K.Knaggs, National Energy Technology Laboratory, U.S. Department of Energy  
Dale F.Stein, Michigan Technological University at Houghton (retired),\* *Committee Chair*  
Robert Williams, Princeton Environmental Institute, Princeton University

##### Group 1—Advanced Separations Techniques

Ramon Espino,\* University of Virginia, *Session Chair*  
Rakesh Agrawal, Air Products and Chemicals, Inc.  
Scott D.Barnicki, Eastman Chemical Company  
Earl R.Beaver, Practical Sustainability  
Liang-Shih Fan, The Ohio State University  
Hugh. W.Hillhouse, Purdue University  
W.S.Winston Ho, The Ohio State University  
Kevin G.Joback, Molecular Knowledge Systems, Inc.  
Harold Hing Chuen Kung,\* Northwestern University  
M.Douglas LeVan, Vanderbilt University  
Nathan S.Lewis, Caltech Chemistry  
Andreas A.Linninger, University of Illinois at Chicago  
Raul F.Lobo, University of Delaware  
Edward J.Maginn, University of Notre Dame  
Richard Noble, University of Colorado  
Babatunde A.Ogunnaiké, University of Delaware  
David Sholl, Carnegie Mellon University  
Jeffrey Siirola,\* Eastman Chemical Company  
Peter Smirniotis, University of Cincinnati  
Michael J.Therien, University of Pennsylvania  
Michael Tsapatsis, University of Massachusetts, Amherst  
Robert Williams,\* Princeton University

##### Group 2—Advanced Subsurface Technologies

John L.Hill III,\* UTD Incorporated, *Session Chair*  
Jay J.Ague, Yale University

Sally M.Benson, Lawrence Berkeley National Laboratory  
Craig M.Bethke, University of Illinois at Urbana-Champaign  
Penelope J.Boston, New Mexico Institute of Mining and Technology  
Corale Brierley,\* Brierley Consultancy LLP  
Peter Dowden, consultant  
Charles Fairhurst, Itasca Consulting Group, Inc.  
William (Bill) L.Fisher, The University of Texas, Austin  
J.Brent Hiskey, College of Engineering and Mines, University of Arizona  
John D.Humphrey, Colorado School of Mines  
Martha Krebs,\* Science Strategies  
Jared R. "Tuck" Leadbetter, California Institute of Technology  
Gregory J.Olson, Little Bear Labs, Golden, Colorado  
Franklin M. "Lynn" Orr, Jr., Stanford University  
Nino S.Ripepi, Virginia Polytechnic Institute and State University  
Michael Q.Pilson,\* University of Rhode Island

### Group 3—Advanced Geochemical Methods

David Keith,\* Carnegie Mellon University, *Session Chair*  
Marc Baum, Oak Crest Institute of Science  
Peter C.Burns, University of Notre Dame  
Ananda Chakrabarty,\* University of Illinois, College of Medicine  
Ronald C.Cohen, University of California, Berkeley  
John William Costerton, Montana State University, Bozeman  
Michael Hoffmann, California Institute of Technology  
Kenneth S.Johnson, Monterey Bay Aquarium Research Institute  
Fred Krambeck,\* Johns Hopkins University  
Klaus Lackner, Columbia University  
Robert A.Larossa, E.I. du Pont de Nemours and Company  
Peter C.K.Lau, Biotechnology Research Institute, National Research Council Canada  
Satish Myneni, Princeton University  
Mark Pasmore, Montana State University, Bozeman  
Eliora Ron, Tel Aviv University  
Daniel P.Schrag, Harvard University  
Jennie C.Stephens, Kennedy School of Government, Harvard University  
John W.Valley, University of Wisconsin, Madison  
Lisa Welp, California Institute of Technology

### Group 4—Novel Niches

George M.Hidy,\* Envair/Aerochem, *Session Chair*  
Thomas Anthony,\* GE Corporate Research and Development  
John R.Benemann, Consultant  
Toby Bradshaw, University of Washington  
R.Malcolm Brown, Jr., University of Texas, Austin  
John B.Carberry,\* E.I. du Pont de Nemours & Company

Zhong-Ying Chen, Science Applications International Corporation  
Vincent L. Chiang, North Carolina State University  
Gary Coleman,\* University of Maryland  
Rathin Datta, Argonne National Laboratory  
Evan Delucia, University of Illinois at Urbana-Champaign  
James Economy, University of Illinois at Urbana-Champaign  
James G. Ferry, Pennsylvania State University  
Richard C. Flagan, California Institute of Technology  
Michael Frenklach, University of California, Berkeley  
John Halloran, University of Michigan  
Mark Holtzapple, Texas A&M University  
Dale W. Johnson, University of Nevada, Reno  
Louis Pitelka, University of Maryland Center for Environmental Science—Appalachian Laboratory  
Tony Sinskey, Massachusetts Institute of Technology  
Dwain Spence, Simteche  
Steven A. Tysoe, GE Global Research Center  
J. Gregory Zeikus,\* Michigan State University  
Hans Ziock, Los Alamos National Laboratory

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\* Member of NRC Committee on Novel Approaches to the Management of Greenhouse Gases from Energy Systems.

## Appendix B

### Workshop Agenda

#### Workshop on Novel Approaches to Carbon Management

National Research Council (NRC)

Board on Energy and Environmental Systems (BEES)

Board on Earth Sciences and Resources (BESR)

*Open Sessions*

February 12–14, 2003

Arnold and Mabel Beckman Center

100 Academy Drive

Irvine, CA

**PURPOSE:** The purpose of the workshop is to identify novel approaches to reducing the net input to the atmosphere of CO<sub>2</sub> from fossil-fuel-based energy systems, including attention to reducing emissions from fossil-fueled systems based on coal, oil or natural gas, biological engineering approaches to carbon removal from the atmosphere, engineering of the entire fuel-cycle system, etc. The concepts, approaches, and research areas that might lead to revolutionary breakthroughs in carbon management identified in the workshop will provide information to DOE to be used to stimulate potential research proposals.

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*February 12, 2003*

7:30–8:30 a.m.      Registration

7:45–8:30          Breakfast

*Plenary Session (Auditorium)*

8:30–8:45          Welcome and Review of Workshop Purpose and Agenda  
Dale Stein, Committee Chairman

8:45–9:10          DOE Perspective  
Michael Knaggs, Scott Klara; National Energy Technology Laboratory

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9:50–9:50	Overview: Global Energy Setting for Carbon Sequestration Bob Williams, Princeton University, Committee Member
9:50–10:20	Morning coffee break
10:20–11:00	Carbon Sequestration: Potential and Risks Sally Benson, Lawrence Berkeley National Lab
11:00–11:25	Carbon Sequestration: Separation Technologies Today Scott Barnicki, Eastman Chemical Company
11:25–11:50	Carbon Sequestration: Storage Technologies Today Charles Christopher, BP
11:50a.m.– 12:30 p.m.	Questions Martha Krebs, moderator, Science Strategies, Committee Member
12:30–1:30.	Lunch

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### Breakout Sessions

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1:30–6:00	Breakout into subgroup sessions (session chair listed in parentheses) <ol style="list-style-type: none"><li>1. Advanced Separations Techniques (Ramon Espino)</li><li>2. Advanced Subsurface Technologies (John Hill)</li><li>3. Advanced Geochemical Methods (David Keith)</li><li>4. Novel Niches (George Hidy)</li></ol>
3:00–3:30	Afternoon Break
6:00	Reception
6:30	Dinner
8:00 & 8:30	Shuttle bus from Beckman Center to hotels
<i>February 13, 2003</i>	
7:45–8:45 a.m.	Breakfast
9:00 a.m.– 12:00 p.m.	Continue subgroup sessions <ol style="list-style-type: none"><li>1. Advanced Separations Techniques (Ramon Espino)</li><li>2. Advanced Subsurface Technologies (John Hill)</li><li>3. Advanced Geochemical Methods (David Keith)</li><li>4. Novel Niches (George Hidy)</li></ol>

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12:00–1:00 p.m.	Lunch
1:00–3:00	Continue subgroup sessions (Breakout Rooms)
3:00–3:30	Afternoon Break
	<i>Plenary Session (Auditorium)</i>
3:30–6:00	Reconvene in plenary session
6:30	Dinner
<i>February 14, 2003</i>	
7:45–8:30 a.m.	Breakfast

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**Breakout Sessions**

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8:30 a.m.– 12:30 p.m.	Continue subgroup sessions
	1. Advanced Separation Techniques (Ramon Espino)
	2. Advanced Subsurface Technologies (John Hill)
	3. Advanced Geochemical Methods (David Keith)
	4. Novel Niches (George Hidy)
12:30 p.m.	Adjourn

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