

Separation and Capture of CO₂ from Large Stationary Sources and Sequestration in Geological Formations

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INTRODUCTION

Following is a discussion of the 2003 A&WMA Critical Review^{1,2} that examined the role of carbon dioxide (CO₂) sequestration in reducing the quantity of greenhouse gases (GHG) emitted to the atmosphere. This is one of the topics being addressed as part of an overall GHG reduction strategy by the Intergovernmental Panel on Climate Change (IPCC).³

In the Review, Dr. Curt White and coworkers contend that CO₂ sequestration in geological formations is necessary, along with other measures, to attain GHG emission reduction goals. The Review concludes that it is practical and feasible to: (1) separate CO₂ from other exhaust gases released by fossil-fuel combustion in stationary sources; (2) capture the CO₂ in gas, solid, or liquid forms; (3) transport the captured gas with negligible escape to appropriate geological formations; (4) inject it into the formations; (5) safely maintain it in formations for hundreds of years with negligible leakage back to the atmosphere; and (6) monitor for public safety and leakage. The Review describes different technologies for each of these topics and evaluates their applicability to specific situations.

Although CO₂ can be practically separated from effluents, captured, transported, and stored, the Review contends that the overall cost of using current technologies must be substantially reduced before they will be widely deployed. Chemical absorbent systems appear to be the most viable option for capturing and separating CO₂ from power-station effluent where partial pressures are low and other gases may interfere. Deep saline aquifers provide the most practical method for long-term storage because they underlie much of the continental United States and would minimize transport costs.

The Review identifies environmental concerns that must be addressed during project planning, construction, and execution. Injection will not be appropriate in areas prone to tectonic activity. Long-term monitoring below and above ground is needed to detect leakage to air and water. The practical applications to date demonstrate that underground CO₂ sequestration provides a safe, verifiable, technologically feasible, and ultimately affordable option to the stabilization of atmospheric CO₂ concentrations.

Four invited and one contributed discussion are presented here. Discussants were charged with stating their

agreement and disagreement with points made in the Review as well as with providing their supporting rationale. They also were requested to add information relevant to the topic. Each discussion is self-contained, and overall joint authorship of this article does not imply that a discussant subscribes to the opinions expressed by the Critical Review committee chairs, the reviewer, or the other discussants. This discussion was compiled from written submissions with revisions by the Critical Review committee chairs for conciseness, clarity, and subsequent review by the coauthors. Substantial deviations from the intent of the discussant are unintentional and can be addressed in a follow-up letter to the *Journal*. Invited discussants are

- Dr. Antonia V. Herzog is staff scientist in the Climate Center at the Natural Resources Defense Council, where she focuses on policies to decrease global warming pollution from power plants, motor vehicles, and major industries and provides information to decision-makers and the public. She is involved in developing federal legislation that would take an integrated approach to reducing carbon (C), nitrogen (N), sulfur (S), and mercury (Hg) pollution from electric power plants. Previously, Dr. Herzog was a Congressional Legislative Science Fellow in the Office of Senator Rockefeller and a postdoctoral fellow at the University of California, Berkeley, in the Energy and Resources Group. She received a B.A. in physics from Vassar College, a B.Eng. from Dartmouth College, an M.S. in applied physics from Columbia University, and a Ph.D. in experimental condensed matter physics from the University of California, San Diego.
- Dr. Sally M. Benson is the deputy director for operations at Ernest Orlando Lawrence Berkeley National Laboratory. Before this position, she served as division director for earth sciences and associate laboratory director for energy sciences at the Laboratory. A groundwater hydrologist and reservoir engineer, Dr. Benson has conducted research to address a range of issues related to energy and the environment, including environmental remediation, gas storage, and geothermal energy production. For the past four years, she has been working on C sequestration, particularly in deep geologic formations.
- Dr. George M. Hidy is an internationally known authority on environmental chemistry and air emissions technologies. He has more than 40 years of experience in environmental science and technology, including management of science and engineering programs in the industrial and academic setting. His work also has extended into the area of climate alteration, with oversight of efforts to promote integrated assessment of climate science to assist policy-makers. He has extensive knowledge of the environmental issues and solutions related to energy production, including electric power generation and the production and use of petroleum-based and renewable fuel sources. Currently an environmental consultant, Dr. Hidy has served as a vice president of EPRI, president of the Desert Research Institute, and professor at the University of Alabama at Birmingham. He is the author or coauthor of more than 100 reviewed publications, including five books.
- Dr. William D. Gunter is a distinguished scientist at the Alberta Research Council and an adjunct professor at the University of Calgary. His expertise is in geochemical processes (stressing use of field data, experiments, and modeling) as they impact on the environment and on the oil and gas industry. Over the past 10 years, he has led combined industry/government-funded projects for geological storage of CO₂ and hydrogen sulfide (H₂S) in aquifers, oil reservoirs, and coal beds. As a result of this, more than 30 publications are available in the public domain on geological storage of CO₂. Dr. Gunter served as a member of the Canadian Federal "Technology Issues" Table on GHG emissions. He currently serves as a member of the Alberta government's "Capture and Geological Storage of GHG Emissions" working group. He is a contributing author on an IPCC special report.

INVITED COMMENTS BY DR. ANTONIA HERZOG

In many respects, the Review provides a comprehensive presentation of the history and current status of projects, technologies, and environmental consequences of CO₂ capture and storage. Yet, the Review jumps to the conclusion that "storage of CO₂ in deep saline aquifers and in deep unmineable coal seams is technically feasible and can have little or no negative environmental aspects." This optimistic assessment, based on only a small number of carefully monitored and verified C storage projects, does not necessarily follow from the information presented. The conclusion needs to more realistically reflect the current status and knowledge of the long-term reliability of large-scale C storage options. There remain significant and continuing challenges for C sequestration that need to be carefully and thoroughly understood and vetted if we are to successfully structure a robust design

strategy and oversight system for long-term C storage. More research combined with a diversity of carefully monitored and verified projects are needed before C storage can be portrayed as either safe or proven, and such research could take several decades to complete.

At present, there remain major environmental concerns. Two of the main ones are: (1) leakage back to the atmosphere over the long term, and (2) the potential for drinking water contamination. While these are issues that could be addressed and dealt with in time, there are now serious questions as to the security and safety of long-term C storage. Significant efforts are going to be required to prove to both the general public and the environmental community the viability of this C management option.

While increasing attention, as exemplified by the Review, is being given to injection of CO₂ into geologic reservoirs, many issues still need to be resolved for geologic C storage to be an effective GHG management technique. In particular, there is the leak-rate performance of the system. Storage sites must be designed to avoid sudden releases, which could pose acute risks through asphyxiation. The more complex challenge is to structure a design strategy and oversight system that not only has the goal of limiting slow leaks to the atmosphere to a de minimis level but is also robust. Future generations may encounter less than perfect performance in real-world operations. To be effective as a C mitigation strategy, geologic storage systems must not leak more than trivial amounts over time spans of hundreds, perhaps thousands, of years. While some individual sites could have varying slow leak rates without undermining the effectiveness of the technique, the system as a whole must be close to leak-free.

What “close to leak-free” means in operation is primarily a function of the degree to which C storage is relied on as a mitigation strategy. One might initially think that the choice of a stabilization target for GHGs would be the strongest driver of the maximum permissible long-term leak rate from the storage system. However, 200–300 years from now, the annual global GHG budgets for stabilization targets between 450 and 750 ppm CO₂ tend to converge at low levels. If large amounts of C are stored over the next several hundred years, the leak rates from the storage reservoirs must remain very low indefinitely to avoid overwhelming permissible emissions for a broad range of stabilization levels. Thus, the cumulative amount of C we store in this and coming centuries has a larger influence on the required performance of the storage system than does the choice of a stabilization target.

For example, if geologic C storage were used for the next 200 years as the exclusive intentional technique to limit CO₂ releases to the atmosphere (i.e., no increase in efficiency and no shift to lower-C energy resources

beyond those assumed in a reference scenario), under any of the “medium” IPCC reference emission scenarios (~1400 gigatons of carbon [GtC] cumulative emissions in the 21st century), a long-term system-wide retention rate of 99.9% still would result in a global emission source ranging between 1 and 2 GtC per year in the year 2200, for stabilization strategies ranging from 450 to 750 ppm (see Figure 1). Such an emission source would represent 20 and 100% of the year 2200 permissible global budgets for stabilization targets of 750 and 450 ppm, respectively. While one hopes the assumption of exclusive reliance on storage is an extreme one, this example illustrates the value of continued emphasis on energy efficiency and increased reliance on renewable energy sources as integral components of a balanced portfolio approach to CO₂ mitigation. Every gigajoule of future high-C energy resources that is displaced with efficiency or renewable energy is that many fewer tons of C that need to be stored and prevented from leaking back into the atmosphere.

While there may be strong theoretical bases to assume effective leak-free long-term operation of C storage systems, such performance will not be demonstrated in real-world conditions for decades. Both to promote public confidence and to manage the risks to future generations from less than perfect storage operations, a sound strategy will embrace accelerated penetration of low-C energy resources and continued emphasis on design of efficient energy production and will use systems as tools to avoid overreliance on C storage programs.

INVITED COMMENTS BY DR. SALLY M. BENSON

The Review addresses most of the important issues regarding the current status and understanding of capture, separation, and geologic sequestration of CO₂. Nevertheless, C sequestration is an immature area of scientific inquiry, and our current understanding about the underlying physical and chemical processes will improve and

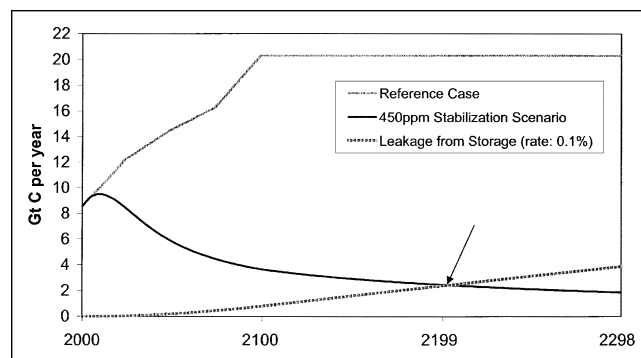


Figure 1. Impact of leaks assuming a 100% C storage with 0.1% leak rate. Leaked CO₂ will equal the total allowable emissions for a 450-ppm CO₂ stabilization level by 2200.

perhaps change significantly over the next decade. It is true that capture, separation, and geologic sequestration are feasible and can begin with today's technology. However, costs are high. All of the separation technologies require a large consumption of energy, which significantly impacts the overall efficiency of electrical generation. Costs and energy consumption may need to be reduced significantly if this is to become the preferred alternative for reducing CO₂ emissions. There are also important geological issues that must be resolved for geologic sequestration to be implemented on a very large scale.

Capacity Assessment

Worldwide estimates of C sequestration capacity are large and suggest that many decades to centuries of CO₂ emissions can be effectively stored in geologic formations. While this is likely to be correct, more research is needed to adequately estimate the capacity and storage efficiency of geologic formations. For example, current estimates of storage capacity are based on the assumption that from 2 to 6% of the pore volume would be available for storage. Recent studies indicate that from 10 to 20% of pore volume may be available. In this case, the storage capacity would be significantly greater and, perhaps more importantly, the "footprint" of an individual project would be significantly smaller. Additional studies are needed that realistically account for the influence of two-phase flow in heterogeneous media and recognize that storage capacity may be a dynamic process that continues to evolve, even after injection is stopped.

Trapping Mechanisms in Brine-Filled Formations

There are at least four important mechanisms for trapping CO₂ in geologic formations: (1) physical trapping below a low permeability seal; (2) solubility trapping; (3) mineral trapping; and (4) residual gas trapping. Often, as in the case of the Review, the important role that solubility, mineral, and residual gas trapping can play is overlooked. These trapping mechanisms contribute to the effectiveness and security of geologic storage and provide a larger number of suitable geologic storage sites.

Experience from Deep Injection of Liquid Wastes and Natural Gas Storage

The Review makes the point that natural gas storage projects, which are to some degree analogous to geologic storage of CO₂, have experienced a number of failures that have resulted in leakage. An extensive review of these projects, and similar experience from deep injection of liquid hazardous waste, indicates that most failures occurred before adequate regulations were in place and that

more recent projects have very high success rates.⁴ In most cases, leakage resulted from poor injection well completions and escape through abandoned wells. New technology for completing injection wells has improved performance, and methods for plugging abandoned wells also are available.

Acceptable Leakage Rates

The Review correctly states that there is a wide range of opinion about the required permanence of geologic storage. Estimates of "acceptable leakage rates" range from 1 to 0.01% per year. The large range reflects different assumptions about parameters such as how much CO₂ will ultimately be stored, the rate of technology innovation, and the cost of CO₂ capture. The Review surmises that a "leakage rate of 0.1% per year could be difficult to achieve in all cases." While this statement is certainly true, particularly if a site is poorly selected, a carefully selected site should be able to achieve or surpass a 0.1% leakage. For example, leakage from oil reservoirs is estimated at 0.00001–0.000001% per year. Storage in these reservoirs and in similar geologic structures should achieve similarly low rates of leakage. Moreover, even if CO₂ leaks out of the primary storage reservoir, dissolution, mineralization, and residual gas trapping will attenuate plume migration and decrease the rate of leakage at the surface.

Monitoring

The Review states, "It is expected that monitoring systems will need to be in place for more than 1000 years after CO₂ injection takes place." An alternative and perhaps preferred approach would be to require that monitoring systems be in place until it is confirmed that CO₂ is safely and effectively stored and will remain so for as long as required. This approach would provide the flexibility to tailor monitoring requirements to site-specific risks. In some cases, where it is quickly demonstrated that the CO₂ is effectively trapped in a secure geologic structure such as a gas reservoir or adsorbed to coal, monitoring would no longer be required. On the other hand, if CO₂ is stored in a structure where it continues to migrate over several decades or centuries, longer-term monitoring may be required.

Regulatory Oversight and Public Acceptance

Regulatory oversight and public acceptance for geologic storage are two of the most critical issues. Even if geologic storage is demonstrated to be safe and effective, without an appropriate regulatory approach and public acceptance, it will not become a preferred option for reducing GHG emissions. While there are some regulations in place today that are relevant to geologic storage of CO₂, additional work is needed to develop comprehensive and

efficient regulatory oversight. The public is, in general, not aware of this technology and has yet to form an opinion about whether they will embrace this approach for reducing GHG emissions. There is a need to begin providing information to the public about the benefits and risks of geologic storage of CO₂. Siting of CO₂ storage projects will need to be managed carefully, with appropriate involvement of the local community, landowners, and government agencies.

INVITED COMMENTS BY DR. GEORGE M. HIDY

The Review represents a comprehensive survey of the state of “conventional” technology for CO₂ emission reductions from stationary sources. It is complemented by at least three other reports that survey similar or additional options.^{3,5,6} Although the Review provides reasonable information about the strengths and weaknesses of different separation and sequestration technologies, it does not provide sufficient detail on cost data to provide for analysis of the different options. This aspect of all of the technology alternatives is key to their application and needs to be elaborated on in future surveys. As noted in the Review, current cost estimates for application of the separation and sequestration technologies to electric-generating stations are considered too high by a factor of 2 or more for practical applications.

Aside from the question of cost, there are certain elements to the GHG issue that complement the Review: (1) general implications of atmospheric GHG concentration stabilization; (2) a policy perspective on sources and the global character of present and future GHG emissions, (3) technology demonstration and practicality; (4) the significance of the transportation share of GHG emissions; (5) the implications of alternate emission reduction strategies, and (6) the implications or consequences of contemporary risk analysis of climate alteration.

Climate Forcing and Stabilization

As the science of climate alteration continues to advance, understanding of the effects of climate forcing by the direct and indirect influence of atmospheric aerosol particles and radiation absorbing gases deepens. The current picture of the variety of atmospheric constituents that affect radiative forcing are listed in the IPCC summaries.³ The list indicates that aside from water vapor, CO₂ contributes an increment of approximately 3 W/m². Other gases, including methane (CH₄), nitrous oxide (N₂O), halocarbons, and ozone (O₃), contribute a similar level of approximately 2.4 W/m². The direct effect of suspended particles is estimated to be on the order of -1 ± 1 W/m². The indirect effect of particles modifying clouds is very uncertain but could be on the order of -1 to $+2$ W/m².

Solar disturbances and contrails from high-flying aircraft may contribute approximately 0.4 W/m².

Simply focusing on CO₂ in a global sense gives insufficient attention to the range of potential forcing that needs to be accounted for in choosing a management path to minimize the potential for climate alteration. Will it be necessary, for example, to set priorities on different forcing contributions to ensure that the optimum choices for GHG management are achieved?

An additional consideration for strategy development is the level of stabilization of GHG concentrations (as CO₂ equivalents) required to deal with potentially negative environmental impacts. The concentration for “stabilization” has been suggested to be in the range of 450–550 ppm CO₂ equivalent by mid-21st century. Stabilization by constraining the rate of GHG emissions rather than atmospheric concentrations has been proposed. In the near term, this appears to create stringent targets for emission controls, especially for the developed nations, and the results may or may not achieve concentration stabilization. The choice and aggressive nature of GHG emission reductions is important not only for availability of technologies but also for minimization of economic disruption.

Policy Perspective on Sources

The evolution of policy for management of CO₂ emissions will be done in the context of international development and commitments. The growth in CO₂ emissions goes hand in hand with population growth worldwide, combined with the demands for energy supply to support industrialization and the “positive” benefits associated with public health and welfare. The current energy supply picture focuses strongly on the worldwide use of fossil fuels, with coal use continuing to grow as a dominant energy source.⁷ Enhancement of energy production through use of renewable supplies and nuclear energy is unlikely to keep up with projected demand through the 21st century. International strategies for CO₂ emission reduction must recognize coal as a dominant energy resource. Coal (and other) technology choices considered by the United States should be readily translatable to the rest of the world. This latter aspect of selecting favored CO₂ reduction technologies was not addressed in the Review.

Different studies have estimated a range of growth in GHG emissions based on various assumptions.^{3,5,6} These estimates show that the principal growth will come from the industrialization of the developing world as contrasted with the developed world. If the projected global growth rates are anywhere near “reality,” policy-makers can expect to deal with annual anthropogenic emissions in the range of 10–20 GtC or more by the mid-21st

century.⁶ This points to the very large amount of CO₂ entering the atmosphere that will need to be at least partially removed and sequestered. A single 1000-MW coal fired plant will generate approximately 1000 tons of CO₂ per hour.⁵ There will be thousands of plants of this equivalent size worldwide. Separation and sequestration of this kind of emissions poses a formidable task, even though the terrestrial reservoir for deep geological storage is believed to be large.^{1,8}

While CO₂ separation from flue gas has been demonstrated on a small industrial and power-plant scale, large-scale sequestration in geological formations, including coal beds and saline aquifers, has not been extensively attempted, as observed by the Review. At the very least, an end-to-end trial of combined separation and sequestration is needed on a large (500–1000 MW or larger) coal-burning power plant to demonstrate that the technology can be operated safely and reliably. While a range of approaches have reached a conceptual design stage, such a major demonstration has yet to be designed and implemented in the United States or elsewhere.

Alternative Technologies

The Review concentrates on postcombustion technologies that represent “off-the-shelf” methods, but it omits several future technological options. The Review explains the separation of CO₂ from other gases is facilitated by liquid solvent absorption, adsorption on zeolites, and the use of high-temperature membrane separators. For conventional coal-fired plants, these technologies probably will require removal of both sulfur dioxide (SO₂) and oxides of nitrogen (NO_x) at relatively low total pressure and low CO₂ partial pressure from the effluent stream before CO₂ treatment. From a practical standpoint, this poses a stringent engineering and cost impact, assuming the chain of processes can be made to operate reliably. Only through practical demonstrations will the highly conservative electric utility industry be attracted to such options.

The uncertainties involved in the retrofit of existing pulverized coal-fired plants has given rise to alternative precombustion technologies, such as coal-based integrated gasification combined cycle (IGCC) plants, followed by decarbonization using a synthesis gas shift of the effluent stream of carbon monoxide (CO) and water.⁹ The shift results in a hydrogen (H)-rich fuel gas with CO₂ at high pressure. Decarbonization then can proceed efficiently using solvent absorption or solid adsorption without the impact of other pollutants. Another precombustion technology that has been proposed is the use of oxygen (O₂) firing (i.e., combustion of fuel in pure O₂, eliminating the handling of N₂ diluent in the flue gas). This latter technology is potentially expensive and has

not yet been demonstrated in the conventional power-plant environment. However, modern IGCC plants have been demonstrated, beginning with the Texaco-EPRI-Southern California Edison Coolwater project in California, and later at the Tampa Electric (FL) and Wabash (KY) plants. Experience from these operations indicates that IGCC has significant advantages over conventional pulverized coal plants for the future, but it is constrained now by higher costs than conventional pulverized coal processing. In the opinion of many, the IGCC technology is the route of power generation in the future, especially if all the acid gases, SO₂, NO_x, toxics, and CO₂, are to be stringently controlled.

If the developed countries are considered alone, the sum of end-use efficiency improvement (EUEI), generation efficiency improvement (GEI), nuclear power, solar and other renewables, and coal use with CO₂ removal appears to be capable of approximately 7 GtC/year reductions. Costs range from savings relative to current use to more than \$100/tC removed.⁶ If the developing countries are considered, little can be achieved in terms of EUEI, but the generation options are similar to the developed world case. The data available in the mid-1990s suggested that the developing world could achieve approximately 7 Gt/year removal at mid-century, at costs ranging from \$900/tC (EUEI) to approximately \$100/tC removed for new-generation technologies, including fossil fuel burning, nuclear, and renewable energy sources. While the Review's cost estimates for CO₂ separation and sequestration appear to be somewhat lower than those projected by Hidy and Spencer,⁶ they remain substantially higher than a level believed to be acceptable in the United States today.

There are other ways to capture CO₂, beyond those specified in the Review, ranging from conventional approaches to extensive air capture combined with mineralization to exotic ideas of manipulation of the reflectivity of the atmosphere.^{8,10} In the 1990s, exploratory work investigated the potential for biospheric capture through terrestrial and marine sources. These approaches recognized the potential for manipulation of the global C cycle as an important adjunct to CO₂ reduction. Experiments have taken place that make use of reforestation, recognizing that young plants have a relatively high capacity for assimilated CO₂ during photosynthesis, but in the longer term, management of the biomass is needed (e.g., biomass fuels or building material). A group of salt-tolerant plants, halophytes, also were explored as a means of using large land areas potentially irrigated with brackish water. The marine biosphere also has been explored for cultivation of seaweed, and stimulation of phytoplankton growth has been explored as a means for CO₂ absorption.⁶

While the biosphere is attractive in many ways for CO₂ removal, there are limitations, both in geochemical potential and in surface storage of biological C, that need to be considered. Terrestrial storage of biospheric C is in the range of 1–2 GtC/year; the upper limit of halophyte farming appears to be approximately 1 GtC/year. Marine systems provide the potential for large storage, based on the world ocean surface area. For example, as much as 7 GtC/year could be stored in seaweed growth, and another 1 GtC/year stored in phytoplankton.⁶ While the terrestrial biospheric options help to remove the target CO₂ emissions, they appear to be much smaller than the marine component, if the latter can be accepted and utilized.

The annual cost of terrestrial vegetation farming ranges from approximately \$100 to \$200/tC removed terrestrially, and for marine “farming” \$100–\$300/tC removed, comparable to or higher than costs for conventional approaches. The biosphere offers the potential for CO₂ management that complements the conventional end-of-chimney or precombustion technologies visualized today. However, implementation of farming strategies would logistically overwhelm practices available today.

Based on knowledge of C reservoirs available geochemically, the oceans offer a major potential for C storage, quite apart from the biosphere.^{6,8} Deep ocean injection of CO₂ has been examined, but the general view today is negative for this option, as it is for manipulation of atmospheric reflectivity. Biospheric manipulation is more practical, but it is negatively viewed because of large uncertainties in the environmental impact of injection, and partly because of concerns about changing the acidity of the oceans’ waters as a result of carbonate chemistry.⁵ This concern and other concerns about the high risks of perturbing marine ecosystems have directed investigators back to terrestrial alternatives and geological sequestration.

The Transportation Element

Electric power generation accounts for approximately one third of the total emissions; another third comes from the transportation sector.³ Estimates or commitments for reduction in the dependency of liquid fossil fuel for transportation appears to be optimistic in the near term. Interest in the electric car, for example, has declined, without the ability to improve battery reliability and with the recognition that CO₂ emission reduction cannot be facilitated without actions controlling the source of electricity. Vehicle fuel efficiency offers an opportunity for CO₂ reduction, but this is offset by the growth in motor-vehicle use worldwide. In the long term, some believe that an H-fueled ground transportation system may evolve.¹¹

An H-based energy system requires large supplies of H and a means of safely distributing and using the gas

analogous to the current liquid fuel system. H produced from natural gas or coal (e.g., IGCC and synthesis gas shift, with CO₂ capture) appears to be an economically viable alternative to H production by electrolysis of water.¹¹ While this direction may be attractive from the point of view of substitution from petroleum fuels for gas and coal in the transportation, it reinforces the need for CO₂ separation and sequestration from large sources, including power plants.

Implications of Risk Analysis

A major factor in the inertia in developing a U.S. GHG climate alteration policy has been the large uncertainty seen by decision-makers in the evidence for climate alteration and its subsequent environmental effects. Tradeoffs between perceived environmental risks and economic risks are also a consideration. Risk analyses began to be reported in the 1990s^{10–12} and showed that added information about climate alteration could substantially improve decision-making if time were allowed to obtain such information.^{13,14} Concepts were developed that called for “integrated assessments” of climate alteration policies.¹² These suggested that the optimal mix between reducing GHG emissions and adapting to incremental climate change based on environmental stress depends strongly on the form of mathematical functions describing “damage.” If damage functions are linear with rising CO₂ levels, the problem is believed to be minor economically; however, if the damages are nonlinear in character (rising at increasing rates with CO₂ levels), a major response to reduce CO₂ emissions is required. Damage functions are conceptually attractive as a means for risk analysis. In practice, environmental risk from climate alteration is difficult to quantify, so little has been accomplished in defining these functions, despite a large and growing research effort.

As a result of concerns about the severe consequences of climate alteration, there has been considerable pressure to develop a “command and control” approach to GHG emission reductions. As an alternative to such a direction, which could create major disruptions in the international energy system, increasing interest has emerged to create a cap-and-trade program. In the United States, some industries have already subscribed to such a scheme.

A recently proposed creative approach¹⁵ would take advantage of the perceived long-term, “sub-chronic” character of climate alteration and develop at a national or provincial level emissions permits, many years worth of which could be issued. They could be used at any time between issuance and the time a target GHG concentration is reached. Because the permits are assets that do not pay a dividend, they would progressively increase in value with time so as to be competitive with similar assets. In so

doing, the value of the permits would follow the estimated value of reductions through the century because stress from climate alteration is projected to change. This approach would provide for wide discretion on the part of emitters to choose options for GHG reductions, while taking long-term advantage of emerging technologies.

Conclusions

The technologies discussed in the Review have not been applied end-to-end to large coal-fired power plants. Different elements affecting policy decisions regarding the reduction of GHG emissions range from strategies for continued delaying actions awaiting "more and better science" to widespread application of biospheric solutions. There is the potential for minimizing environmental risk and the need to "force" modern energy-generation technologies into use. It would seem prudent to expedite at least one complete demonstration of existing separation and sequestration technology on a conventional power plant. The initial cost of such a demonstration will be sufficiently large to require at least partial government support, as exemplified by the U.S. Department of Energy's Clean Coal program. Such a program takes considerable time to complete, so this action should not be delayed further if reliable technology is to be considered in the next decade.

INVITED COMMENTS BY DR. WILLIAM D. GUNTER

Although the Review is thorough in the topics covered, it did not include enhanced oil recovery and depleted oil and gas reservoirs in its discussion of capture and storage options. This discussion elaborates on coalbed CH_4 and geochemical reactions followed by a general discussion of geological traps for CO_2 , migration, leakage, and monitoring in the context of sedimentary basins. Such considerations are important in formation of the protocol for the new industry of geological sequestration.

The terminology in the Review, although consistent with U.S. usage, does not represent a generally accepted international usage. In "biological sequestration," CO_2 is extracted from the atmosphere by photosynthesis in the growth of plants. The process of CO_2 capture and storage takes place in one step with no transport involved between steps. In "geological sequestration," the process starts at the industrial point sources where the CO_2 is "captured" from the waste gas stream. It is then compressed to a liquid form and transported by pipeline to a site where it is injected into deep geological media for permanent "storage." Geological sequestration refers to the complete process of capture through storage, not just the storage process as implied in the Review. Suitable geological media for storage are only found in

"sedimentary basins," which consist of thick piles (i.e., 1–10 km thick) of consolidated sediments, which are also the source areas of fossil fuels and are distributed throughout the world. The production of oil and gas by the petroleum industry from reservoirs where the fossil fuel is trapped in portions of the sedimentary basin frees up the pore space that the oil and gas formerly occupied. This pore space can be used for storage of CO_2 . Other geological media that are candidates for storage are deep saline aquifers which are discussed in the Review.

Coalbed CH_4

The Review advanced 10 working hypotheses for possible effects that may occur when injecting CO_2 into coal. These hypotheses are based on results taken from other areas of coal research and may or may not be applicable to coalbed sequestration. Coal has very different properties than other reservoir rocks (i.e., sandstone and carbonates) with respect to its sorption and swelling properties, which can hinder or help the production of CH_4 and storage of CO_2 . The Review cites experiments performed at elevated pressure and zero effective stress that indicate plasticization of coal taking place at greatly depressed temperatures in the presence of high CO_2 pressures near pressure and temperature conditions expected to be found in deeper coalbed reservoirs. However, because these experiments were carried out at zero effective stress, the glass-to-rubber transition temperature would be at a maximum depression. In geological media, the weight of the overburden would apply a principal stress much greater than the reservoir fluid pressure, resulting in a substantial effective stress that leads to less swelling of the coal compared with zero effective stress. Elastic models for stress behavior of coal and the resulting effect on porosity and permeability¹⁶ have been applied to the field with success.¹⁷ Caution is urged in extrapolating laboratory results directly to the field when the experimental conditions are substantially different. These 10 hypotheses should remain as hypotheses until evaluated under field conditions.

Mineral Reactions

The Review contends that solubility trapping is enhanced by the dissolved CO_2 reacting with the reservoir or aquifer rock. Carbonate (CO_3) minerals will dissolve congruently when attacked by carbonic acid (H_2CO_3) formed during solubility trapping, creating more bicarbonate (HCO_3) ion as opposed to the undissociated acid, thus increasing the capacity of the formation water for CO_2 . Normally, there is not much reaction before equilibrium is reached. This is not the case for basic silicate minerals, which react incongruently by forming a secondary precipitate or precipitates, thereby allowing much larger amounts of reaction before equilibrium is reached.¹⁸ The final result

may be formation of an HCO_3 brine plus a more acid aluminosilicate mineral as in the case of reaction with a basic potassium aluminosilicate mineral (e.g., potassium feldspar to muscovite) or a CO_3 mineral precipitate and acid aluminosilicate mineral as in the case reaction with a basic calcium aluminosilicate material (e.g., calcium feldspar to kaolinite and calcite). It is not sufficient to just have a calcium (Ca)-rich brine to precipitate calcite when CO_2 is dissolved in the brine. As the Review points out, a base is also needed. This point is often misunderstood.

CO_2 Migration, Trapping, and Leakage

Concern has been expressed over the rate of leakage of CO_2 to the surface once it has been injected into the storage reservoir. There are a variety of traps that operate at different scales and different levels of security.¹⁹ The following discussion adds details not included in the Review. At pore sizes on the scale of millimeters in addition to residual gas trapping, there are geochemical traps that can take the form of sorption in coalbed CH_4 reservoirs, solubility trapping in oil or water, and ionic trapping (when the CO_2 dissolved in the water through solubility trapping reacts with the minerals present in the geological media and becomes HCO_3 or CO_3 ions in formation water). If the concentration of CO_3 or HCO_3 builds up sufficiently in the water, precipitation of a CO_3 mineral can occur; this is "mineral trapping," the most secure type of geochemical sequestration. Ionic trapping is second because it reduces the amount of CO_2 that would be released from the water if a pressure drop occurred compared with solubility trapping.

Reservoir-scale traps (i.e., km in size) are the classic petroleum traps related to the geology of a sedimentary basin and have been formed by either stratigraphic or structural events during the formation of a basin. Hydrodynamic traps are found in saline aquifers that are basin-scale in size (i.e., hundreds of kilometers) and are formed by the plumbing infrastructure of the sedimentary basin caused by the juxtaposition of permeable (e.g., sands) and impermeable (e.g., shales) sediments, with later folding and faulting during the formation of the basin. Movement of CO_2 injected into these hydrodynamic traps will be controlled by the regional flow regime in the sedimentary basin, which is usually on the order of cm/year or less, and may occur as a pure CO_2 supercritical phase or as CO_2 dissolved in the formation water by solubility trapping. It is expected that most of the CO_2 will be in the latter form after several pore volumes of movement. In a sedimentary basin, such as the Alberta Basin in Canada, CO_2 injected into and dissolved in a deep aquifer would take more than a million years to migrate to the surface along the aquifer flow path. During that time, the other smaller-scale trapping mechanisms discussed previously

would have the opportunity to take effect. Migration along these natural flow paths is predictable because they have been operating over geologic time. In contrast, potential short circuits exist to these regional flow paths along existing faults or abandoned wellbores. These present the biggest risk and must be carefully evaluated and monitored.

Monitoring

Monitoring of CO_2 geological storage is necessary to identify unexpected major leaks caused by short-circuiting, early enough to mitigate them and lower their impact. Because the geological storage reservoir is below 800 m depth, leaks may not reach the surface. In addition to the smaller-scale trapping mechanisms, there exists a series of barriers and aquifers above the storage target, each of which forms an independent hydrodynamic trap. Consequently, monitoring must take place at different depths—in the storage media (i.e., reservoir or saline aquifer), above the storage media in other hydrodynamic traps, and at the surface. A broad range of monitoring tools must be used that are either applied remotely (e.g., 4 days seismic) or in situ via a well drilled through the volume to be monitored (e.g., geochemical). Because monitoring can be costly, a monitoring plan must be devised that is economically feasible but that reduces the risk of undetected major leakage. Fortunately, the risk of rapid leakage drops off with time and may be directly related to pressure and permeability. Before injection of CO_2 into a target reservoir or aquifer, the designated geological storage media should have been established to have a past geological history of minimal leakage, and the initial fluid pressure should be known. The risk of fluid leakage at this point is at a minimum. As soon as injection of CO_2 is started, the pressure will rise, reaching a maximum at the end of injection when the geological medium has reached its storage capacity. After injection ceases, the pressure will decay over a period of time, stabilizing at a new low pressure. Injection would normally be on the order of tens of years, while the decay would take place over hundreds of years. Monitoring frequency would mirror the pressure buildup and decay curves (which are directly related to leakage rate), terminating after 100 years except for regional monitoring activities.

Outlook—A New Industry: Geological Sequestration

The tools developed by and the experience of the oil and gas industry over the past 50 years make geological sequestration of CO_2 an attractive and feasible but not inexpensive option. The cost of CO_2 capture is still high. If sequestration utilized, the cost of fossil-fuel energy use will increase, which will allow renewable energy to

become more competitive while lowering CO₂ emissions. Geological sequestration can become a new industry, with geological surveys providing “top-down” analysis identifying the best volumes of sedimentary basins for storage.²⁰ The regulatory agencies can build on existing oil and gas regulations to put in place safe practices to be followed for storage. Experience can be gained in injection and storage from existing and historical enhanced oil recovery (EOR) projects, and from disposal of other wastes into saline aquifers. “Tag-on” monitoring projects to commercial operations (e.g., Sleipner, Weyburn) can also be very important for evaluating monitoring tools and procedures. Natural analogs, which are natural CO₂ reservoirs that have held CO₂ for millions of years, are being characterized as examples of secure storage. Public outreach is needed to have geological sequestration accepted for industry, an economic incentive such as an emission trading system has to be sanctioned by government to make this option viable.

CONTRIBUTED COMMENTS OF

DR. STANLEY J. PENKALA

It is unlikely that human efforts to reduce atmospheric CO₂ levels through conservation, increased energy efficiency, and sequestration will be successful because: (1) anthropogenic CO₂ sources are only a small portion of global CO₂ emissions; (2) natural CO₂ sources are not static but are apparently increasing; (3) not all anthropogenic sources are required to curtail CO₂ emissions; and (4) not all anthropogenic sources are included in the IPCC inventories. Figure 1 of the Review purports to demonstrate correlation between relate anthropogenic CO₂ emissions and atmospheric CO₂ as measured at Mauna Loa. By shifting the zero baseline of the emissions graph and adjusting the relative scales of the concentrations and emissions, the two curves are made to run parallel to each other for the past 50 years. If anthropogenic CO₂ emissions were driving atmospheric concentrations, then the breakpoint of both graphs should have occurred at essentially the same time, not 20 years apart. If 1.0 GtC/year emissions produced an increase of 23 ppm CO₂ between 1850 and 1950, then the addition of 5.0 GtC/year between 1950 and 1990 should have produced an increase of 115 ppm, not the 60 ppm CO₂ observed.

Anthropogenic sources in developing countries are not currently required to curtail their CO₂ emissions, even though their contribution to the global anthropogenic CO₂ inventory will exceed any curtailment possible by the industrialized nations under the constraints of the Kyoto Accord. The IPCC inventory understates agricultural CO₂ emissions from field burning on the grounds that the CO₂ released by burning will be taken up by new vegetation in the next season. This is only true if the same

acreage and vegetation were under cultivation each year. This is doubtful, because feedstock and grain consumption increases with growing populations throughout the world. The IPCC inventory excludes CO₂ emitted by human respiration and by the respiration of domesticated animals raised by humans as sources of meat, milk, and raw materials (hides, bone, etc.). The average emission rate of each human is approximately 500 kg CO₂/year. With a global population of 6 billion in 2000, expected to increase to 9 billion by 2050, this source of CO₂ is not static. At this time, the human respiration source alone would increase the IPCC anthropogenic inventory by 10–15%.

Although the proposed sequestration schemes are technologically feasible and will reduce CO₂ emissions, the cost will be high with respect to any expected benefit. The money spent on these attempts to control CO₂ and, by implication, to control global warming would be better spent in mitigation efforts to control adverse effects of any global warming that might result. Beneficial effects might include increased growing seasons and decreased winter fuel usage in northern climes.

RESPONSE FROM DR. CURT M. WHITE ET AL. CRITICAL REVIEW AUTHORS

In response to Dr. Herzog's assertion that the Review is overly optimistic about sequestration based on small number of projects, we emphasize examples such as Sleipner and Weyburn in the Review. CO₂ has been successfully captured from large point sources and sequestered in the geosphere. CO₂ has also been successfully sequestered in a deep unmineable coal seam in New Mexico. Although additional successful projects are desired, none of these projects had any significant environmental consequences, The Review's conclusion that “these have little or no negative environmental aspects” is also valid based upon the data available.

We agree with Dr. Benson's observations that current estimates of the capacity of various geological CO₂ sinks need to be substantially refined. The estimates of CO₂ storage capacity for individual deep saline aquifers and coal seams may be even more imprecise than she indicates. For example, there is little information on the location, depth, lateral extent, or physical and chemical properties of deep unmineable coals. Not only do we lack that basic information, we do not have reliable information on their CH₄ content.

The Review covered three trapping mechanisms: (1) hydrodynamic trapping (what Dr. Benson calls physical trapping below a low-permeability seal); (2) solubility trapping, and (3) mineral trapping. As Dr. Benson observes, the Review did not discuss residual gas trapping.

With respect to monitoring, we believe that at least initially, we should plan to monitor for very long times. Once we are comfortable that the CO₂ remains securely in place and that the leak rate is very low, we may want to reevaluate the need for long-term monitoring or decrease the monitoring frequency.

Dr. Hidy provides a useful discussion of costs that complements the Review. The full-scale demonstration project he describes is badly needed. The FutureGen Integrated Sequestration and Hydrogen Research Initiative is a \$1 billion dollar government/industry partnership to design, build, and operate a nearly emission-free, coal-fired electric and H₂ production plant (www.netl.doe.gov/coalpower/sequestration/futureGen/main.html). This will be an end-to-end application of advanced technologies to generate both electricity and H₂, as well as to capture the CO₂ and store it in the geosphere.

We disagree with Dr. Hidy's proposal to force modern energy-generation technologies into use. IGCC and other modern electric power-generating technologies have been shown to have much higher efficiency and lower emissions. One would think that the electric power-generating community would flock to these technologies, but they have not. In 2001, there were 340 new power plants under various stages of planning and permitting. None were IGCC plants. According to the Gasification Technologies Council in 2001, less than 10 new gasification facilities were planned for the United States by 2005. Forcing the electric power-generating community to build these plants is not desirable. Providing incentives for them to build and operate these high-efficiency low emission plants is the better path.

Dr. Gunter clarifies the usage of certain terms in different countries. We agree with his statements concerning mineral reactions, CO₂ migration, trapping and leakage, and monitoring, as well as his points on "Outlook—A New Industry: Geological Sequestration."

Dr. Penkala believes that natural CO₂ emissions will dwarf efforts to reduce manmade emissions. There is much uncertainty concerning the relative contributions of natural vs. anthropogenic sources as indicated in the Review's introduction. This uncertainty was not the focus of this Review and should be addressed elsewhere.

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