

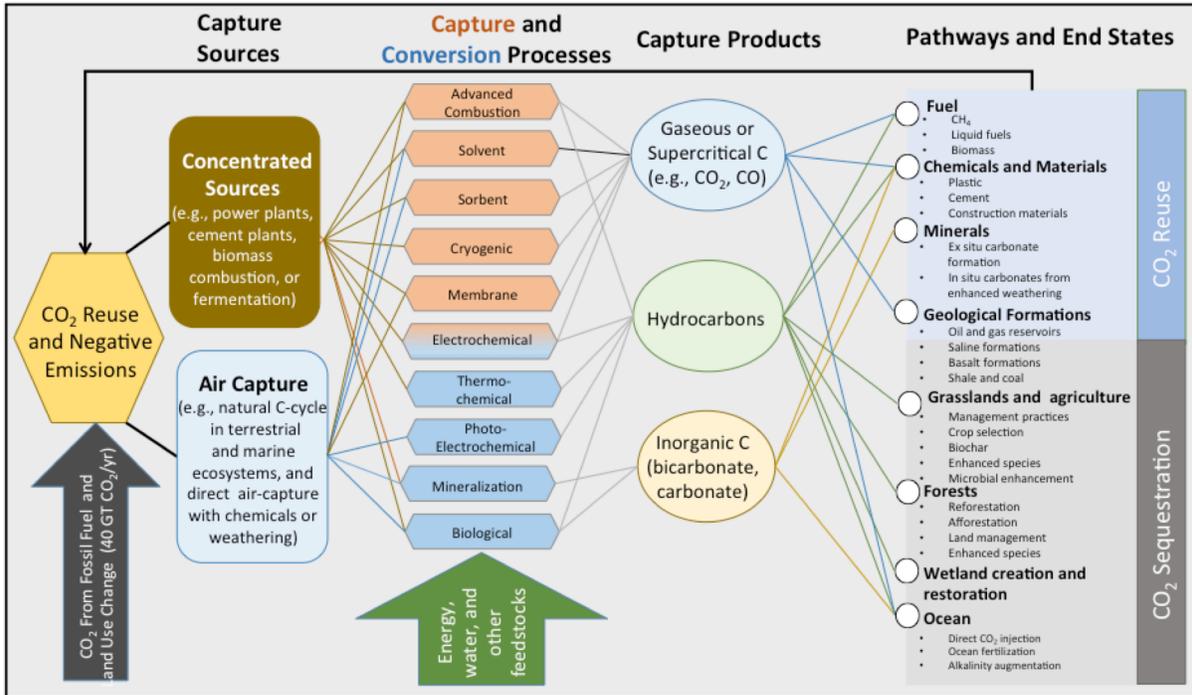
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LETTER REPORT FOR: Secretary of Energy Ernest J. Moniz  
FROM: SEAB CO<sub>2</sub> Utilization Task Force  
SUBJECT: Task Force on RD&D strategy for CO<sub>2</sub> Utilization and/or  
Negative Emissions at the gigatonne scale  
DATE: November 28, 2016

You charged the SEAB CO<sub>2</sub> Utilization Task Force (**Appendix 1**) to describe a framework for a Department of Energy (DOE) Research, Development and Demonstration (RD&D) program on CO<sub>2</sub> utilization technologies that has the potential to reduce CO<sub>2</sub> emissions and/or introduce negative emissions at the gigatonne (Gt) scale (**Appendix 2**). This letter report presents our findings based on Task Force deliberations and discussions with the relevant offices within the DOE. This is an Interim Report, which has been reviewed by a group of experts (**Appendix 1**) in this area who have offered suggestions that have improved the report.

At the outset, it is important to define what negative emissions and CO<sub>2</sub> utilization mean and imply. We first note that global warming is caused by radiative forcing that depends on the concentration of greenhouse gases (GHG) such as CO<sub>2</sub> in the atmosphere. The concentration increases when the rate of GHG emissions from the earth is higher than the rate of GHG absorption by the earth, thus producing a net increase in emission rate. In this report, we will focus on those technologies that have the potential to introduce ~1 GtCO<sub>2</sub> per year of *net* decrease in global emissions to the atmosphere. Currently, the total global emissions are ~40 GtCO<sub>2</sub>/yr, and therefore 1 GtCO<sub>2</sub>/yr of reductions represent 2.5 percent. The net decrease in emissions must involve consideration of the whole global system, natural and engineered, which is highlighted in this report.

Looking at the global energy system, it is increasingly clear that there are viable options to reduce emissions in the electricity sector, although their implementation would require serious combination of policy measures and technological advancements. However, given the distributed nature of the emissions, lack of viable alternatives at scale and a variety of other factors, it is more difficult to do the same for the



**Figure 1.** The negative emission and CO<sub>2</sub> utilization option landscape. Options exist for the capture source, capture and conversion processes, capture product, sequestration repository, and the engineering approach to achieve negative emissions. Cross-cutting research opportunities exist across the entire negative emissions landscape.

transportation and the industrial sectors. Hence, negative emissions and CO<sub>2</sub> utilization are worth considering as a counteractive measure as long as there is a net decrease in emissions. Furthermore, if the atmospheric CO<sub>2</sub> concentration rose above any dangerous threshold with zero net emission rate, technologies for negative emissions could play an important role to reduce the atmospheric concentration from increasing beyond that threshold.

Many options for CO<sub>2</sub> utilization and negative emissions have been proposed. For example, negative emissions using BECCS (Bio-energy conversion with CO<sub>2</sub> Capture and Storage (CCS)) involves using photosynthesis to capture CO<sub>2</sub> from the air, biomass conversion to energy, CO<sub>2</sub> capture from the flue gas, and storage in deep geological formations. Likewise, zero-net carbon CO<sub>2</sub> utilization can be achieved by directly separating CO<sub>2</sub> from air using a chemical capture process and adding carbon-free energy to convert it into a fuel. There are dozens of such pathways that have been

proposed for negative emissions and CO<sub>2</sub> utilization. Instead of addressing each of the proposed options separately, we propose the holistic framework provided in Figure 1. This framework recognizes that each pathway fundamentally requires choosing whether CO<sub>2</sub> will be captured from the air or a concentrated source, a capture and/or conversion process to convert CO<sub>2</sub> to a form that can either be utilized or sequestered and, finally, utilization as an economically valuable product or sequestered to remove the CO<sub>2</sub> from the atmosphere. Undoubtedly, the number of pathways makes this a complex issue since each pathway requires numerous questions about rates, locations, amounts, costs, infrastructures, chemical form, use, re-use, and fate of carbon, all of which need to be addressed systematically. Given this complexity and the short period of time that the Task Force had for deliberation, we were unable to delve into all aspects of this important topic. Hence, what we offer in this report is not an exhaustive list of recommendations, but rather five main recommendations where the Task Force believes RD&D can make the biggest difference. Our recommendations on the RD&D areas fall in two categories:

**CATEGORY 1 - Approaches with a higher degree of confidence regarding scalability and RD&D opportunity.** The Task Force offers five specific recommendations in this letter report relating to CATEGORY 1 opportunities. The scientific justification for these recommendations can be found in the Appendices of this letter report.

**CATEGORY 2 - Approaches that deserve consideration, but for which there is a lower degree of confidence regarding scalability and RD&D opportunity.** The Task Force identifies two topics in CATEGORY 2. These topics deserve deeper consideration than can be offered here.

We also recommend a series of future workshops to shed light on both these categories and form the basis for a comprehensive RD&D strategy for the community at large.

We highlight a few features that provide a framework for our recommendations.

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1. Our recommendations are addressed to the scientific community at large, with the hope that DOE will lead an effort in the future, involving other agencies and organizations as appropriate.
2. The criterion of  $\sim 1$  GtCO<sub>2</sub>/yr scale leads to some important considerations that are worth stating (**Appendix 3**):
  - a. To appreciate the magnitude of GtCO<sub>2</sub> per year, it is noteworthy that only a few industries match that scale today, such as steel, concrete, agriculture, as well as coal, oil and gas. These industries pervade our economy and have taken decades to develop. Hence, creating the infrastructure needed to manage GtCO<sub>2</sub> per year presents an unprecedented significant challenge.
  - b. Any process that captures, transports, and converts  $\sim 1$  GtCO<sub>2</sub>/yr will require significant amounts of carbon-free energy<sup>1</sup>. Hence, the global demand for carbon-free energy will increase faster than it would without the use of negative emissions and CO<sub>2</sub> utilization technologies.
  - c. There are some applications that may not be at the GtCO<sub>2</sub>/yr scale today, but are close enough and of much higher carbon value to provide a pathway to the GtCO<sub>2</sub>/yr scale for other applications<sup>2</sup>. Furthermore, it is unlikely that a technology could be scaled to 1 GtCO<sub>2</sub>/yr if it would be a stretch for the technology to be scaled to 0.1 GtCO<sub>2</sub>/yr. Hence, RD&D areas ought to focus on those technologies that could reasonably easily be applied at least at the scale of 0.1 GtCO<sub>2</sub>/yr. All of these considerations point to the need for a roadmap to achieve the GtCO<sub>2</sub>/yr scale.

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<sup>1</sup>A barrel of oil equivalent contains about 6.1 GJ or 1.7 MWh of energy. Hence, to convert CO<sub>2</sub> into a barrel of oil equivalent, the lower bound for the amount of carbon-free energy needed will be 1.7 MWh. In 2015, the US used 7.08 billion barrels of oil. If all the carbon in this came from CO<sub>2</sub>, then the lower bound for the amount of carbon-free energy needed would be 12,000 TWh, which is about 41 Quads. As a comparison, the U.S. uses roughly 100 Quads per year of primary energy. Also, the total electricity generation in the US in 2014 was 4093 TWh, out of which 1340 TWh came from carbon-free sources (nuclear, wind, solar, hydroelectric).

<sup>2</sup>If CO<sub>2</sub> was to be used as the source of all carbon in the global annual production of plastics (311 million tonnes (MT) per year in 2014), it would consume about 0.8 GtCO<sub>2</sub> per year. By 2030, the annual global plastic production is expected to rise to 700 MT, which would require roughly 490 MtC/yr or about 1.8 GtCO<sub>2</sub>/yr. See **Appendix 6** for more details.

- d. To achieve 1 GtCO<sub>2</sub>/yr, it is important to consider RD&D in a holistic way, one that bridges fundamental science with systems engineering and includes the feedback loops and iterations at various stages in between. The cost and economics of the technology options are important considerations for RD&D (**Appendix 3**).
- e. Deployment for a 1 GtCO<sub>2</sub>/yr scale requires capabilities and large-scale investments that can only be achieved by the private sector. It also involves regulatory compliance and business models, posing complex execution challenges. The choice of how scaling is achieved and how this landscape is navigated has implications for how rapidly the cost can be reduced down a techno-economic learning curve and how risks are managed for large-scale investments (**Appendix 3**). It is important to consider this context for RD&D since it will likely be involved at almost all aspects of this landscape.
- f. An endeavor at this scale will inevitably have consequences, intended and unintended, on our biosphere. Many of these consequences are difficult to predict *a priori*. It is critical that the RD&D has a continuous effort to understand the consequences of the GtCO<sub>2</sub>/yr-scale of net decrease in emissions so as to minimize the ill effects and maximize the positive impacts. This will require a robust and widespread monitoring program of our climate and biosphere.
- g. Such an endeavor will require a continuous supply of skilled people, implying that education of a large workforce will be important.
- h. Finally, it seems inevitable that to achieve 1 GtCO<sub>2</sub>/yr scale, there will need to be a charge on CO<sub>2</sub>, either through a price or via regulations or a combination of both. We do not dwell on this issue at all in this report, since the policy landscape is still evolving. Rather, we focus on the RD&D strategy that should be in place now in order for the world to get prepared early and not wait for a carbon charge to be created and adopted.

We note that negative emissions and CO<sub>2</sub> utilization are not new topics for the scientific community. There have been several recent noteworthy reports, articles and papers in the past<sup>3,4</sup>, some resulting from past DOE workshops<sup>5</sup> and meetings. So what is new in this letter report?

Even though negative emissions and CO<sub>2</sub> utilization technologies affect the carbon balance on earth in different ways, rarely have they been jointly considered under a single unifying framework. Most of the past reports focused on individual technologies (e.g., bioenergy and carbon capture and storage (BECCS); direct air capture of CO<sub>2</sub>; or transforming CO<sub>2</sub> into fuel) and estimated their multidimensional impact on land use, water use, energy use, capital and operating costs, etc.<sup>6</sup> This report addresses the issue with a “systems approach” involving coupling between natural and engineered carbon pathways, which are described in detail in **Appendix 4**. The systems approach is essential to understand whether these technologies introduce a *net* decrease in global CO<sub>2</sub> emissions, and if so roughly how much. Furthermore, past works have typically considered how current technologies will improve in cost and performance over time and scale, i.e. going down a known techno-economic learning or experience curve. Following your charge to this Task Force, we address the questions:

1. Where can RD&D make the biggest difference to create new techno-economic learning curves or significantly expedite existing ones when scaled to ~ 1GtCO<sub>2</sub>/yr?
2. What is the multidimensional framework for understanding the positive and negative impacts for the choice of RD&D?

Here are the recommendations in Category 1.

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<sup>3</sup> Fifth Assessment Report of the Intergovernmental Panel on Climate Change (2014)

<sup>4</sup> M.K. McNutt et al., *Climate Intervention: Carbon Dioxide Removal and Reliable Sequestration*, National Research Council Report, The National Academies Press (2015).

<sup>5</sup> *Carbon Cycling and Biosequestration – Integrating Biology and Climate Through Systems Science*, Report of the DOE Office of Biological and Environmental Research (2008)

<sup>6</sup> P. Smith *et al.*, “Biophysical and economic limits to negative CO<sub>2</sub> emissions,” *Nature Climate Change* **6**, 42–50 (2016).

**Recommendation 1 – Systems Modeling:** Carbon fluxes between the natural systems - atmosphere, land, oceans – and commercial systems – electricity/heat, transportation, industry – have to satisfy the laws of nature, with the commercial system having to satisfy the imperatives of economics as well. While the laws of nature (thermodynamics, kinetics of phase equilibria, carbon reactions, mass transport, etc.) are universal, the imperatives of economics are designed by humans and vary across the world. The laws of nature and economic relationships both invariably introduce non-linearity in the system, which could be potentially ignored at small scale, but would be risky to do so at the GtCO<sub>2</sub>/yr-scale. This makes predictions of the overall system behavior, such as net negative emissions, very difficult. While our goal is to reduce overall emissions and decarbonize the atmosphere at the GtCO<sub>2</sub>/yr-scale, the choices will likely have a wide range of ecological consequences. Some environmental impacts will be positive and will be seen as co-benefits; others will force trade-offs and may be seen as potential show-stoppers. New scientific understanding is likely to be required in order to provide estimates of central values and uncertainties in each area of environmental concern.

Given this complexity of both natural and engineering pathways for carbon in our biosphere, the Task Force recommends intensification of research programs that build on and expand today's effort to create a constellation of systems models of the global carbon balance at different degrees of spatial and temporal resolutions. This modeling goes beyond today's integrated assessment models, which do not consider the full impact of all technological pathways in engineered systems at the GtCO<sub>2</sub>/yr scale. Such a tool will be essential to:

- a) Provide a framework to guide our holistic thinking about carbon management.
- b) Model the complex interactions involved in the global carbon balance that could lead to predictions of non-linear systems behavior that cannot be foreseen today.
- c) Develop approaches to systematically study parametric sensitivity and quantify uncertainties of different variables and their collective impact on policy making.
- d) Allow researchers to explore “what if” scenarios and thereby identify individual or combinations of technological pathways, both existing as well as new and disruptive,

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that would produce large net positive (or negative) GtCO<sub>2</sub>/yr-scale effects on carbon while minimizing the adverse ecological impact. Such an approach could use 0.1 GtCO<sub>2</sub>/yr as a filter to further evaluate the potential for scale up to 1 GtCO<sub>2</sub>/yr. Furthermore, it could also identify multiplier effects as well as dead ends for various technological pathways that may not be obvious otherwise.

- e) Identify performance and cost targets that would shape a RD&D strategy for these technological pathways.
- f) Develop a roadmap to expedite scale-up of technologies and infrastructure to accelerate negative emissions and CO<sub>2</sub> utilization to the GtCO<sub>2</sub>/yr scale.

Complementary to the research effort in systems modeling, we also recommend to:

- g) Emphasize or create an effort for global data collection and analysis to validate the predictions of the models.

Details of the scientific justification can be found in **Appendix 4**. We also recommend that the scientific community should be brought together in a workshop to identify the details of the research program proposed here.

A systems approach that combines carbon science and systems engineering could become an important tool for policy making. However, it would take time to develop and refine. We should not wait for such a tool to be fully developed to identify some reasonably obvious RD&D areas of interest. The Task Force recommends a few other RD&D topics in Category 1 that should be initiated soon.

**Recommendation 2 – Harnessing the Natural Biological Carbon Cycle:** The largest flux of carbon (~120 GtC/yr or 440 GtCO<sub>2</sub>/yr) between the atmosphere and land occurs via photosynthesis in plants. Roughly 2-3 percent of this carbon remains stored on land for decades, while the rest is emitted back to the atmosphere. Could this natural biological carbon cycle be harnessed to absorb more carbon from the atmosphere, store more carbon on land, or use a combination of both to produce negative emissions? Could this be achieved as a positive co-benefit of increasing productivity of crops for food, bioenergy, feed and fiber that the world will need, and thereby be of commercial value? We believe that these questions deserve increased research to explore and develop the following capabilities. The scientific justifications can be found in **Appendix 5**:

- a) Increase the photosynthetic efficiency<sup>7</sup> and optimize crops for food, bioenergy, feed, and fiber, as well as trees used for bioenergy, reforestation and afforestation, with no marginal increase in resource inputs, such as fresh water, fertilizers, and pesticides, and preferably with reductions in each of these.
- b) Rigorously evaluate the benefits and limitations of marine macroalgae as a bioenergy feedstock for both land-based energy (e.g., for BECCS) as well as for liquid transportation fuels.
- c) Identify approaches to reduce decomposition of soil organic carbon and N<sub>2</sub>O emission impact by taking into account the biology and chemistry of soil carbon decay. Examples include creating roots that go deeper in the rhizosphere with higher lignin content.
- d) Optimize crops and management technology that stabilize organic carbon over longer time frames including accelerating the transition to no-till agriculture, sustaining no-till land after the transition is made and extending the period in which forests are net CO<sub>2</sub> sinks.

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<sup>7</sup> It should be noted that among the most innovative and potentially high-impact strategies to improve photosynthesis in plants is to import carbon concentration mechanisms that operate in photosynthetic bacteria and algae. The opportunity is clear but the molecular technology to import these complex components is lacking, as is a full understanding of the biology of their assembly.

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- e) Because of the complexity of the biosphere, intensify research in understanding the ecological impact of harnessing the natural biological carbon cycle, including using systems modeling (**Appendix 4**) to understand the net global carbon impact.

**Recommendation 3 – Synthetic Transformations of CO<sub>2</sub>:** Carbon dioxide can be transformed into a variety of chemicals and fuels that have commercial value. The lower bound for the energy needed to achieve this is the energy released from combusting these chemical and fuels to form CO<sub>2</sub>. Hence, synthetic transformations of CO<sub>2</sub> require significant carbon-free/neutral energy in the form of heat and/or electricity, which can often be the dominant cost. The commercial value of the chemicals and fuels determine the upper bound for the energy and other feedstock costs. Furthermore, these transformations need to follow one or a combination of chemical pathways – electrochemical, photochemical, biochemical, thermochemical – with sufficient efficiency and low infrastructure costs to produce market-competitive chemicals and fuels. To achieve this, it is necessary to create a coherent RD&D program to:

- a) Reduce the cost of delivered carbon-free/neutral exergy (electricity and high-temperature heat) with a target range below 3 cents/kWh.
- b) Focus on fundamentals of electrocatalysis and photoelectrocatalysis to identify catalysts made of abundant elements that reduce the overpotentials required for redox reactions (e.g., CO<sub>2</sub> reduction and the O<sub>2</sub> evolution reaction) at high reaction rates.
- c) Identify materials for thermochemical redox reactions that operate below 1000 °C and are thereby compatible with today's infrastructure in the chemical industry.
- d) Identify and genetically manipulate biological organisms that use non-photosynthetic biocatalysis for CO<sub>2</sub> fixation into chemicals and fuels.
- e) Create new systems architecture and designs for chemical reactors that leverage the research on materials and organisms for CO<sub>2</sub> transformations, and are scalable to the GtCO<sub>2</sub>/yr scale while meeting the cost targets to make cost-competitive chemicals and fuels.
- f) Based on scaled engineered systems analysis in (f), use systems modeling of the global carbon balance (**Appendix 4**) to identify opportunities and challenges for the availability of feedstock, infrastructure, and processes (**Appendix 8**) needed for GtCO<sub>2</sub>/yr scale impact.

Scientific details and follow-on workshop recommendations are in **Appendix 6**.

**Recommendation 4 - Carbon Dioxide Sequestration in Geologic Formations:**

Geological storage of CO<sub>2</sub> is an important piece of the puzzle for negative emissions since it has the potential to store at GtCO<sub>2</sub>/yr. Over the past decade, several programs have been created to explore RD&D of CO<sub>2</sub> storage in saline aquifers. By its very nature, this has no commercial value. On the other hand, industry is using CO<sub>2</sub> for traditional enhanced oil recovery (EOR), which has commercial value for CO<sub>2</sub>. However, because of the cost to purchase CO<sub>2</sub>, the incentives in EOR are aligned to minimize CO<sub>2</sub> use and maximize hydrocarbon recovery.

If the incentives were changed (e.g., via a carbon charge), would it be possible to create a non-traditional EOR in a way that valued the CO<sub>2</sub> storage (perhaps reaching GtCO<sub>2</sub>/yr scale) and simultaneously retained the commercial value for the produced hydrocarbons? Could such non-traditional EOR lead to net reduction in CO<sub>2</sub> emissions? If the EOR sites and saline aquifers are co-located, would such formations offer a continuum of opportunities for CO<sub>2</sub> storage while also creating value out of CO<sub>2</sub>? While these questions have been asked before, they have not been fully addressed via RD&D programs. Furthermore, while much research has focused on the fundamentals of CO<sub>2</sub> mineralization in rocks, its scalability to the GtCO<sub>2</sub>/yr scale remains undeveloped.

In view of the importance of CO<sub>2</sub> storage to create negative emissions and the possibility of simultaneously creating value out of CO<sub>2</sub>, the Task Force makes the following recommendation in four categories:

Cross-Cutting Issues:

- a) Develop and execute on a roadmap for accelerating CO<sub>2</sub> storage and reservoir utilization from high-purity anthropogenic CO<sub>2</sub> emission sources where there are some immediate opportunities<sup>8</sup>.
- b) Create and support a Data Commons<sup>9</sup> as a shared resource for the research community to document CO<sub>2</sub> injection, storage, oil recovery, brine recovery and any

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<sup>8</sup> Studies have identified that there are high-purity sources at the scale of 30 MtCO<sub>2</sub> that can be captured at \$30/tCO<sub>2</sub>. [http://energy.gov/sites/prod/files/2016/09/f33/DOE%20-%20Carbon%20Capture%20Utilization%20and%20Storage\\_2016-09-07.pdf](http://energy.gov/sites/prod/files/2016/09/f33/DOE%20-%20Carbon%20Capture%20Utilization%20and%20Storage_2016-09-07.pdf)

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other relevant information that would be helpful to collectively understand and investigate effective co-optimization and storage techniques.

- c) Develop and implement a monitoring, measurement, and verification system capable of accurately predicting multiple century CO<sub>2</sub> leakage rates and environmental impacts of carbon capture, utilization, and storage (CCUS) projects. This is essential to increase the confidence needed by all stakeholders (e.g., project operators, financiers, regulators, insurers, and communities) to initiate and sustain the rapid scale-up of GtCO<sub>2</sub>/yr scale reservoir utilization and saline formation storage.

### Reservoir Utilization:

- d) Intensify and expand the RD&D program to:
  - i. Continue to improve fundamental understanding of mechanisms of pore scale CO<sub>2</sub> displacements, including immiscible displacements and other novel CO<sub>2</sub>-EOR schemes, and flow in a broad class of reservoirs beyond CO<sub>2</sub>-EOR.
  - ii. Co-optimize CO<sub>2</sub>-EOR and CO<sub>2</sub> storage in hydrocarbon reservoirs and underlying saline formations.
  - iii. Develop an approach to estimate reservoir storage costs and operating parameters for different types of reservoir systems.
  - iv. Estimate infrastructure needs such as pipelines between storage sites and CO<sub>2</sub> sources, and create a roadmap in terms of costs, rates and timings for scale-up.
- e) In the absence of a carbon emission charge, conduct jointly funded pilot-scale and demonstration projects with the hydrocarbon industry and research community (academic and national laboratory) to test co-optimization techniques and expand the range of hydrocarbon reservoirs where CO<sub>2</sub> storage is attractive. Put all of the quality assured data from these project into the Data Commons consistent with the requirements of the contract.

### Saline Formations:

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<sup>9</sup>Data sharing could be obligatory for all government contracts and joint studies involving government funding. Special provisions need to be made to protect propriety data from oil and gas-field operators. Responsibilities of data users should be clearly spelled out in access agreements. Compliance on the part of data generators and users should be monitored for compliance with the access policies

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- f) Continue and strengthen the R&D program to understand and harness secondary trapping mechanisms, site characterization, and geomechanical effects to assure safe and effective GtCO<sub>2</sub>/yr-scale storage on century to millennium time scales.
- g) Address important questions on leakage (or integrity of seals), accuracy of models for long-term performance, risk of seismicity, efficacy of monitoring to detect leakage and groundwater contamination.

### In-Situ Mineralization

- h) An expanded R&D effort is needed to determine whether or not our fundamental understanding of CO<sub>2</sub> mineralization offers GtCO<sub>2</sub>/year potential for carbon sequestration. Convening a team of scientists and engineers to identify the full range of opportunities and challenges is a logical first start.

The scientific justifications for these recommendations are provided in **Appendix 7**.

**Recommendation 5 – Carbon Dioxide Capture and other Separation Technologies:**

It is important to create pure feedstocks of CO<sub>2</sub> and other forms of carbon for both utilization and storage. However, CO<sub>2</sub> generally comes in mixtures with other gases, such as in the exhaust of fossil-fuel power plants or the atmosphere. To overcome the entropy of mixing, the separation of CO<sub>2</sub> from a gaseous mixture or the separation of carbon in liquid form (e.g., methanol) from a mixture of miscible liquids can become highly energy intensive. Depending on the source or application, the capital and operating costs of separation can often dominate the total cost of CO<sub>2</sub> transformation (**Appendix 6**) or storage (**Appendix 7**). The Task Force makes the following recommendation for RD&D to reduce these costs:

- a) Identify new, low-cost CO<sub>2</sub> sorbents made of abundant elements that have a binding enthalpy  $|\Delta H| < 70$  kJ/mol, binding rate constant  $k_f > 12000$  M<sup>-1</sup>s<sup>-1</sup>, and  $k_f \gg k_r$ , where  $k_r$  is the rate constant for the unbinding or dissociative reaction. A lower enthalpy correlates to lower energy costs whereas higher binding rate constant correlates to smaller plant size and thereby lower capital costs. Current sorbents are have either: (a) high rate constants and high binding enthalpy, and thereby high energy costs; or (b) low rate constants and low enthalpy, and thereby high capital costs.
- b) Identify new, low-cost, noncorrosive, non-viscous liquid solutions with lower heat capacity than water that selectively bind CO<sub>2</sub> with the characteristics in (a).
- c) Discover new materials and processes to separate miscible liquid mixtures optimized for low capital and operating costs.
- d) Design, build and demonstrate scalable reactor designs that offer the possibility to substantially reduce carbon capture and separation costs.

The scientific justifications for these recommendations are provided in **Appendix 8**.

Below are the topics in Category 2 that the Task Force feels are worth deeper exploration in the future.

1. **Direct Air Capture (DAC) of CO<sub>2</sub> Using Chemicals:** This topic has received recent attention from the scientific community<sup>10</sup> where it was estimated that it could cost about \$600/tCO<sub>2</sub> to capture CO<sub>2</sub> directly from the air. The Task Force believes that it is worth exploring through research the practical lower limits of DAC costs. Since today's sorbents lead to cost estimates of \$600/tCO<sub>2</sub>, this will necessarily involve research into high-performance sorbents. Without advances in sorbent performance, it is highly unlikely that the costs will be substantially reduced. The scientific foundations of this are well described in **Appendix 8**. Another aspect of this challenge relates to systems integration and the capital and operating costs associated with it. This is described in **Appendix 9**. If overall DAC costs could be credibly brought down below \$200/tCO<sub>2</sub> at scale through R&D, DAC could potentially become cost effective for negative emissions if the carbon is utilized to create high-valued products such as plastics, where the cost of energy could be significant.
2. **Mineralization in Oceans:** There have been suggestions that one could induce CO<sub>2</sub> mineralization in oceans at the GtCO<sub>2</sub>/yr scale. The reaction of CO<sub>2</sub> + H<sub>2</sub>O → H<sup>+</sup> + HCO<sub>3</sub><sup>-</sup> does not require any energy input. The bicarbonate anion (HCO<sub>3</sub><sup>-</sup>) can react with cations such as Na<sup>+</sup> or Ca<sup>++</sup> to form bicarbonate or carbonate salts. However, the remaining proton (H<sup>+</sup>) reduces pH, which manifests as ocean acidification. This is thought to represent a threat to the marine environment that could potentially be mitigated by the introduction of alkaline materials into the ocean<sup>11</sup>. Scalable approaches to form bicarbonate or carbonate materials would require large supplies of alkaline salts to neutralize the acidity. While alkaline rocks such as basalt and serpentine do exist, getting the alkaline materials to mix with

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<sup>10</sup> R. Socolow et al., Direct Air Capture of CO<sub>2</sub> with Chemicals, APS Report (2011). <http://www.aps.org/policy/reports/assessments/upload/dac2011.pdf>

<sup>11</sup> R. Albright, Hosfelt J., Kwiatkowski L., Maclaren J.K., Mason B.M., Nebuchina Y., Ninokawa A., Pongratz J., Ricke K.L., Rivlin T., Schneider K., Sesboüé M., Shamberger K., Silverman J., Wolfe K., Zhu K., Caldeira K. (2016). Reversal of ocean acidification enhances net coral reef calcification. *Nature*. DOI 10.1038/nature17155

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water and form salts requires significant infrastructure and materials at scale. This has been well covered by a recent NRC report<sup>4</sup>. The Task Force did not have adequate time to explore other routes to induce mineral formation without acidifying the oceans. Hence, we feel this topic deserves a deeper look. But it is worth emphasizing that we must be very cautious in modifying the ecology of the oceans, since the complex interactions with our food chain and our environment are not completely understood.

Below is a list of all the Appendices accompanying this letter report.

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**APPENDIX 1**  
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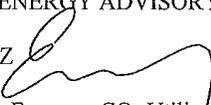
**APPENDIX 2**  
**CHARGE TO THE TASK FORCE**



**The Secretary of Energy**  
Washington, DC 20585

June 7, 2016

MEMORANDUM FOR THE CHAIR  
SECRETARY OF ENERGY ADVISORY BOARD

FROM: ERNEST J. MONIZ   
SUBJECT: Establishing a Task Force on CO<sub>2</sub> Utilization

I request that you form a Secretary of Energy Advisory Board (SEAB) Task Force composed of SEAB members and independent experts to describe a framework for a Department of Energy (DOE) Research, Development, and Demonstration (RD&D) program on CO<sub>2</sub> utilization technologies that have the potential to reduce CO<sub>2</sub> emissions and/or introduce negative emissions at the gigatonne (GT) scale.

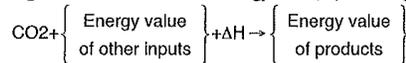
Global energy related CO<sub>2</sub> emissions are approximately 35 GT per year representing about 70% of anthropogenic GHG releases. CO<sub>2</sub> captured from fossil fuel electricity generating plants, industrial facilities, or removed from the atmosphere can be: (1) stored for a geological time period in deep saline aquifers; (2) converted into biomass; and (3) upgraded to useful chemicals.<sup>1</sup>

The Task Force will review on-going activities in the DOE, industry, national laboratories, academia, and non-profits and identify new opportunities for research and cooperation between different disciplinary research groups. This charge could perhaps be achieved by sponsoring a SEAB Workshop.

**Schedule:** The Task Force will make a preliminary presentation at SEAB's September 2016 meeting. The Task Force will present its final letter report at SEAB's December 2016 meeting. This Task Force is expected to carry out most of its work in sessions open to the public.

**Designated Federal Officer:** Karen Gibson, Director, Office of Secretarial Boards and Councils

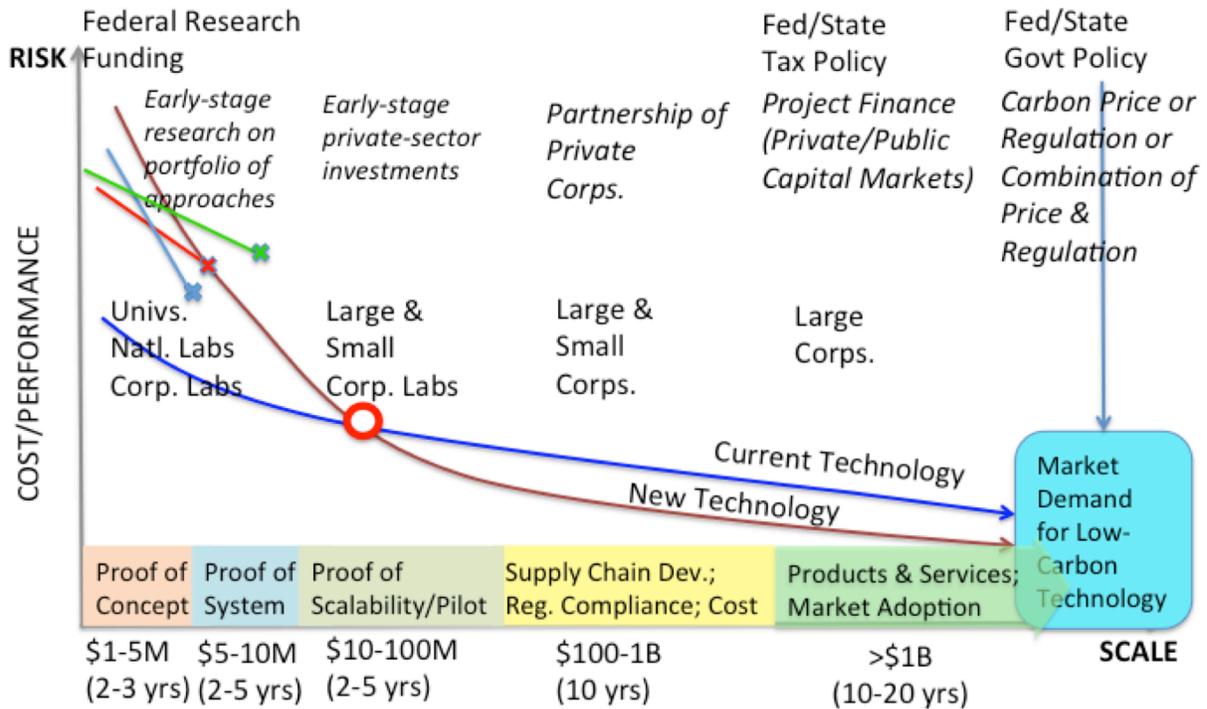
<sup>1</sup> Because CO<sub>2</sub> is a product of combustion (oxidation), upgrading to a higher value chemical compound (reduction) is necessarily subject to the following constraint: the amount of energy added, Q must be greater than ΔH.



To be economic, the value of the products must be greater than the cost of the inputs plus the cost of the energy, Q. Any CO<sub>2</sub> emission from the energy production, Q, must be netted out.

**APPENDIX 3**  
ROADMAP FROM RD&D TO GIGATONNE SCALE

The journey of any energy and environmental technology from a research laboratory to gigatonne (GtCO<sub>2</sub>/yr) scale impact involves many stages and facets – science, engineering, economics, finance, pilot demonstration, regulatory compliance, supply chain development, infrastructure development, business models, market structures as well as federal, state and local policies. While there are exceptions to the rule, this journey generally takes 10-20 years and involves large amounts of financial capital. The activity in the stages are not linear but interrelated, so this needs continuous use of science and engineering to de-risk a technology and reduce its cost down a techno-economic learning curve. While such curves generally follow a decreasing cost curve with scale, as shown in Fig. A3.1, this is not always true (see below). Hence, it is worth exploring what determines the shape of this curve and where does RD&D play a role.



**Figure A3.1** Process of scaling from research to gigatonne scale expressed as techno-economic learning curves. New technologies can out-compete current technologies if they are less costly, or have superior performance or offer new services and capabilities. Research based on science and engineering is needed at all stages of this scaling process.

Early-stage fundamental research, which is needed for discoveries and inventions, is mostly funded by the federal government. The scientific community as a whole pursues a portfolio of approaches in this “proof of concept” phase with the hope that a few of them would lead to major advances in technologies. The research occurs largely at universities and national laboratories, but some are conducted in research laboratories of corporations as well. Each research project may last about 3 years and cost \$1-5M. While much of this fundamental research may not directly result in breakthrough technologies, they produce much-needed insights, understanding, shared learning and a scientific knowledge base that is of immense value to the whole scientific community and is utilized in ways that are often unforeseen. Hence, continued funding of such fundamental research is a key ingredient for a vibrant ecosystem.

When a few of the these “proof of concept” breakthroughs show promise, a team of scientists and engineers builds a first prototype of an engineered system that offers insights into future viability in terms of performance and costs. This “proof of system” also occurs in laboratories of universities, national laboratories and corporations. This proof of system requires about 2-5 years and costs roughly \$5-10M. These investments are often shared between the federal government and the private sector. It is at the end of this stage that the private sector can identify commercial value of a technology by envisioning products and services. If this occurs, the private sector is best positioned to advance this technology to show proof of scalability via pilot projects. Such a development requires investments of \$10-100M and needs about 2-5 years as well. This stage is best led by the private sector with enabling science and engineering coming from national laboratories and universities. The U.S. is very productive in the proof of concept, proof of system and the pilot demonstration phases compared to other countries. Many observe that the U.S. is better at creating new technology options than scaling and implementing them.

If the pilot demonstration is successful, the next stage involves supply chain development; first-of-a-kind commercial plant design, construction, and operation;

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meeting regulatory compliance (e.g., National Environmental Policy Act); and further cost reduction for market competitiveness. This stage can take about 5-10 years and can cost \$100M-1B. As has been proposed, this is best achieved by the private sector, perhaps through partnerships between companies in a supply chain such that the costs, risks, and rewards are shared (Majumdar et al, 2016). A private sector innovation project is much more likely to lead to deployment of the technology than one run by the federal government. The reason is that the federal government does not have the experience or “feel” of private market investment decision-making and operations management.

At the end of this stage, an infrastructure that is commensurate with commercial scale deployment at the GtCO<sub>2</sub> scale can be built. By its very nature, such a deployment must involve products and services in a market and generate revenues to pay for the upfront and operating costs. GtCO<sub>2</sub>-scale deployment requires large-scale financing of multiple projects, with each project on the order of \$1B. The cost of capital is a key element of the cost of products and services. Furthermore, they have long tenors. Such large-scale, low-cost, and long-term financing involves access to private and public capital markets, which are influenced by federal and state tax policies. For example, master limited partnerships (MLPs) have been widely used to aggregate capital in the public stock market to finance infrastructure construction (e.g., pipelines) in the fossil fuel sector. The tax policy involved in MLPs enables financing at very low cost of capital. Such a provision needs to be broadened beyond the fossil fuel sector to enable low-cost financing of low-carbon technologies that should include negative emissions and CO<sub>2</sub> utilization projects.

Deployment will also be influenced by federal and state policies on promoting low-carbon technologies, which could occur through a carbon charge - either via a carbon price in a market, via regulations on carbon emissions, or via a combination of both. Since capital formation and market deployment occurs largely by the private sector, it is very important that the federal and state policies on finance, markets, and regulations are predictable and have long-term certainty so that the private sector can plan



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The process of scaling during the commercial phase often follows a behavior  $C = \alpha\theta^n$ , where  $C$  is the cost per unit,  $\theta$  is the cumulative production,  $\alpha$  is the cost of the first unit produced and  $n$  is an experience or learning parameter related to the learning rate,  $LR = 1 - 2^n$ . The speed of scaling is captured by the parameter  $n$  and, thereby, LR; higher magnitudes of  $n < 0$  leads to higher LR. Figure A3.2 shows learning curves for solar photovoltaics (IRENA, 2012) and nuclear energy (Grubler, 2010). Learning curves of other energy technologies can be found in Rubin et al. (2015).

As observed in Fig. A3.2, LRs can vary a lot and depend on a number of factors. For example, low LRs can be attributed to:

1. underinvestment in research to enable the scaling process from fundamental science to commercial operations;
2. incompatibility with current infrastructure, thereby creating need for new infrastructure to be built;
3. lack of technological headroom for performance and cost improvements;
4. inadequate access to low-cost long-term financial capital;
5. lack of market structures and regulatory frameworks that encourage business competition;
6. lack of or shortages in supply chains;
7. time-consuming regulatory process involved in licensing, siting, and permitting;
8. lack of governance, unfavorable labor conditions, and their impact on project execution;
9. the inability and unwillingness to take small and calculated risks to reduce costs; and
10. the change in inflation rate and cost of capital.

The case of nuclear power technologies is noteworthy because  $n > 0$ , implying  $LR < 0$  or negative learning rate. This is due to a combination of reasons related to the regulatory process, the lack of modularity in plant construction (or the variability in each plant) and risk aversion in the nuclear sector. A negative LR for a low-carbon technology can make a technology uncompetitive, which could then be displaced by

technologies that may be economically competitive but have high emissions. On the other hand, modular technologies such as photovoltaics (PVs) are generally more tolerant to risks since the size of investments in modules is relatively low compared to those involved in gigaWatt-scale plants. This allows for more trial-and-error iterations and rapid learning to improve the technology. Furthermore, competition in the market can dramatically increase the LR. Part of the PV favorable cost experience has been a progressive decline in unit margins due to increased competition. Science and engineering research is used as a competitive advantage. Its utilization is often more effective when directly applied to improve small and modular technologies, something that is very difficult to achieve when large-scale plants are designed, constructed and operated. This also leads to rapid learning (high value of LR). But unforeseen events, such as accidents caused by natural forces or intentional/unintentional human intervention, can also stymie a whole sector, as has been observed in nuclear power.

Hence, when one is thinking of RD&D strategies to achieve GtCO<sub>2</sub>/yr-scale in an expedited way, it is very important to consider creating an ecosystem with plenty of feedback loops of information and knowledge flowing back and forth along this process. For example, although fundamental research focuses largely on deepening and broadening our scientific understanding, they must be conducted in the context of solving a GtCO<sub>2</sub>/yr-scale problem in order to identify and expedite the translation process to reduce cost and/or improve performance. Furthermore, the late-stage technology development ought to include mechanisms whereby fundamental understanding can accelerate cost reduction and performance improvements at the pilot and commercial stages. The use of such contextual RD&D can accelerate progress down a techno-economic learning curve.

What is the role of government policy? It should be evident from Fig. A3.1 that it plays multiple roles. Government funding of early-stage fundamental research in the proof of concept and proof of system stages is critical. Government policy on carbon price or regulation or a combination of both can create demand and competition for low-carbon technologies, thus driving the whole ecosystem. Government policy on finance (e.g.,

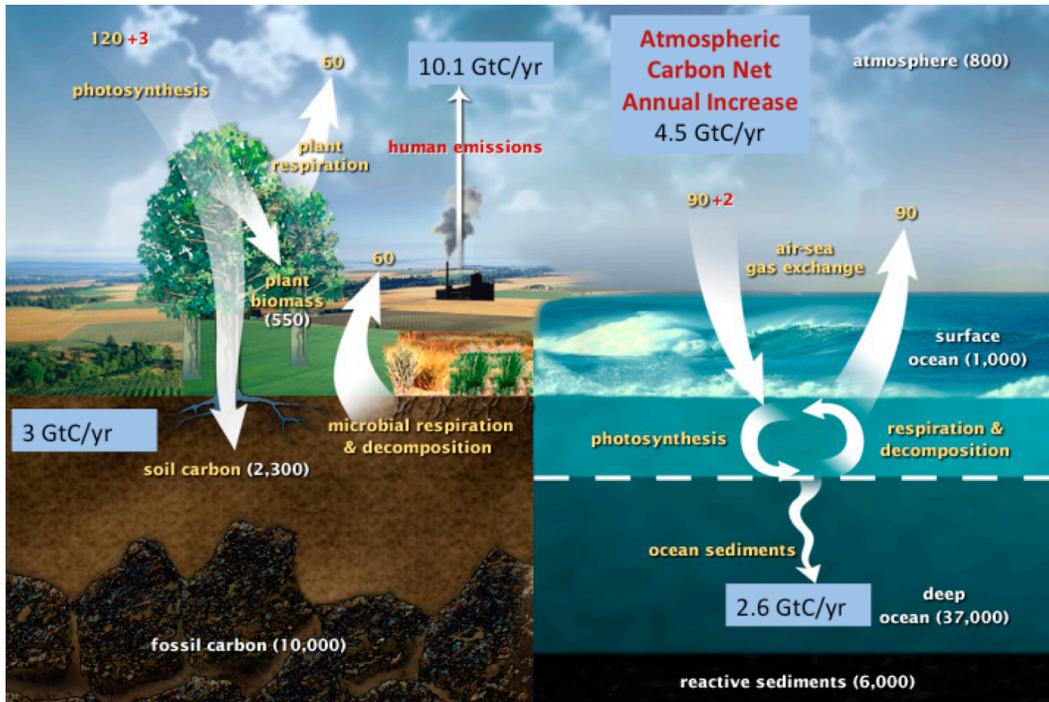
tax policy) can enable low-cost, long-term financing that is needed to build infrastructure. Finally, its role in convening and working closely with the private sector to expedite regulatory compliance (e.g., NEPA) as well as catalyze partnerships and ecosystems is important as well.

## References

- Grubler, A., 2010. The costs of the French nuclear scale-up: A case of negative learning by doing. *Energy Policy* **38**, pp. 5174-5188.
- IRENA 2012. Renewable energy technologies: Cost analysis series – Solar Photovoltaics, Vol. 1, Issue 4/5. Report from the International Renewable Energy Agency.
- Majumdar, A., J.M Deutch, N.R. Augustine, G.P. Shultz, 2016. [Energy innovation needs new private sector push](#), *Bloomberg View*, Feb 11.
- Rubin, E.S., I.M.L. Azevedo, P. Jaramillo, S. Yeh, 2015. A review of learning rates for electricity supply technologies. *Energy Policy* **86**, pp. 198-218.

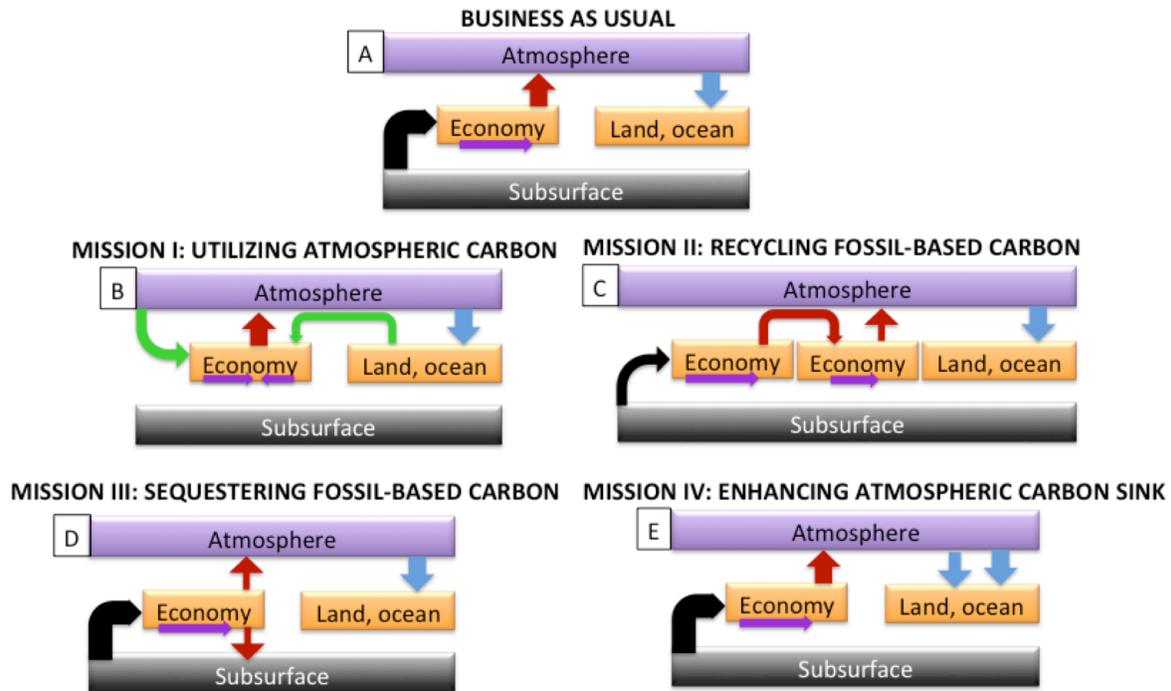
## APPENDIX 4

### UNIFYING FRAMEWORK FOR NEGATIVE EMISSIONS AND CO<sub>2</sub> UTILIZATION



**Figure A4.1** The global carbon cycle with 2005-2014 average values shown in boxes (The Global Carbon Project, 2015). <http://www.globalcarbonproject.org/about/index.htm>. Based on an original image from <http://earthobservatory.nasa.gov/Features/CarbonCycle/>. The units are given in GtC/yr whereas the report uses GtCO<sub>2</sub>/yr. Note that 1 GtC/yr is equivalent to 3.67 GtCO<sub>2</sub>/yr.

The system involving the global carbon balance is complex, due to the presence of large carbon fluxes between the atmosphere, the land biosphere, and biota and water in the near-surface ocean, as depicted in Fig. A4.1. Prior to the growth of the global economy, these three carbon pools were in approximate equilibrium, averaged over a year. But today there is an imbalance in the fluxes as a result of the extraction of hydrocarbon fuel from a stock of geological carbon that would otherwise be isolated from the active pools, its use as an energy source via combustion, and the immediate dispersal of its waste product, CO<sub>2</sub>, to the atmosphere. The anthropogenic modifications of the natural carbon cycle produce small changes in the total annual fluxes, but nonetheless the interplay between various technological pathways could produce unintended consequences that cannot be easily foreseen.



**Figure A4.2:** Schematic representation of the current fossil fuel economy (Business as Usual, Panel A) and four missions (Panels B, C, D, and E) that could reduce CO<sub>2</sub> emissions to the atmosphere, relative to the current fossil fuel economy. Panel B (Mission I): Use carbon from the land or atmosphere; Panel C (Mission II), recycle combustion-generated CO<sub>2</sub>; Panel D (Mission III), prevent combustion-generated CO<sub>2</sub> from reaching the atmosphere; Panel E (Mission IV), enhance the land and ocean CO<sub>2</sub> sinks.

A schematic of the current carbon flows in the global economy is seen in Figure A4.2, Panel A. Fossil fuel is extracted from the subsurface (black arrow), used by the economy (purple arrow), and its carbon is emitted to the atmosphere as CO<sub>2</sub> (red arrow). Also shown in this panel is the carbon flow from the atmosphere to the land and ocean (blue arrow), which mitigates the build-up of atmospheric CO<sub>2</sub>. These land and ocean “carbon sinks” currently remove CO<sub>2</sub> from the atmosphere at approximately half the rate at which human beings are emitting CO<sub>2</sub> to the atmosphere by burning fossil fuels.

In all, there are four arrows in Panel A of Figure A4.2. In the other four panels, one of these arrows is modified. Each change represents a mission that is an objective of current R&D.

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- a) Mission I (Panel B) features extraction of carbon feedstock from the land biosphere or the atmosphere, rather than from fossil fuels. An example is the use of biomass instead of fossil fuel for energy – the carbon in the biomass having been fixed from atmospheric CO<sub>2</sub> by photosynthesis.
- b) Mission II (Panel C) enables the recycling of the CO<sub>2</sub> after combustion so that emission to the atmosphere is delayed and CO<sub>2</sub> emissions from another sector is displaced. An example is the capture of CO<sub>2</sub> at the exit of a fossil-fuel plant or an industrial facility and converting it into carbon-based fuels for transportation, thus using the carbon in fossil fuels twice. The external energy required to convert CO<sub>2</sub> back to hydrocarbons (reversing combustion) must come from a low-carbon source. Moreover, the system as a whole must have net advantages over using the same low-carbon energy source to either: 1) displace the fossil-fuel based power generation, letting the transportation fuel be made from petroleum; or 2) produce a suitable low-carbon transportation fuel directly (e.g., solar hydrogen), letting the fossil-fuel plant emit its CO<sub>2</sub> without capture. Regardless of which pathway one adopts, the transportation fuel (liquid fuel or electricity) must be competitive in the market.
- c) Mission III (Panel D) directs CO<sub>2</sub> emissions to a destination other than the atmosphere, such as below ground. An example is the capture of CO<sub>2</sub> from the flue gas at a coal or natural gas power plant and its sequestration in a geological formation.
- d) Mission IV (Panel E) increases the strength of the land or ocean carbon sink. An example is the deliberate modification of agriculture to store additional carbon in the soil.

Business as usual and the four missions are elaborated in Figure A4.3. There are seven boxes. The global economy is represented as three boxes instead of one: “electricity and heat” (Box 1, largely, for residential and commercial buildings), transportation (Box

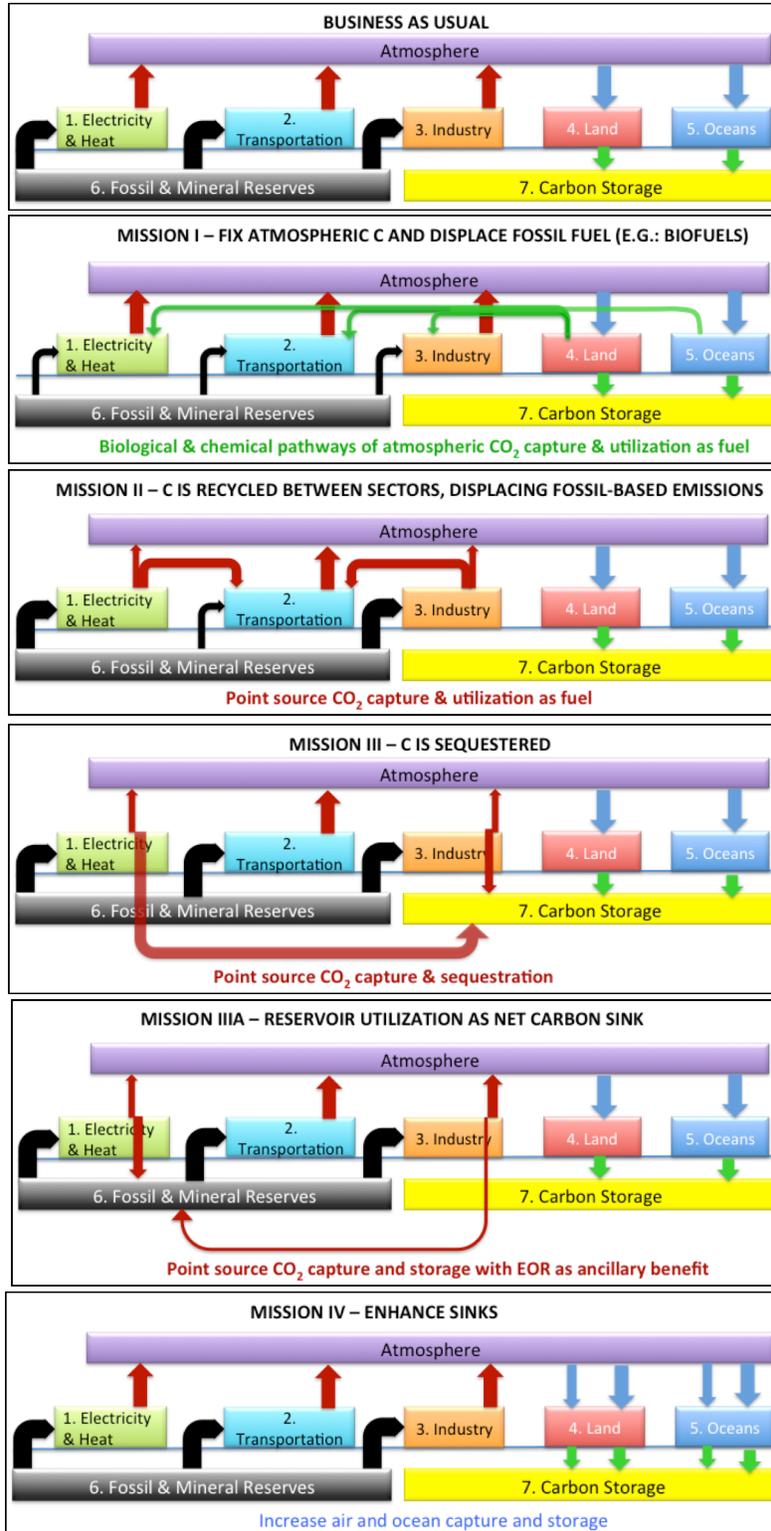
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2), and industry (Box 3). The land sink (Box 4) and the ocean sink (Box 5) are presented separately. The subsurface is divided into sites with fossil and mineral reserves (Box 6) and without these reserves (Box 7). As for the four missions:

- a) In Mission I (second panel from the top), carbon from land biomass and from the atmosphere partially substitutes for fossil fuels.
- b) In Mission II (third panel), some of the byproduct CO<sub>2</sub> in the production of electricity and heat for buildings and industry (Boxes 1 and 3) is recycled to the transportation sector (Box 2), and as a result less fossil fuel is required for vehicles.
- c) In Mission III, CO<sub>2</sub> produced from buildings and industry – but not the transportation sector – is stored below ground either without performing a separate function (fourth panel) or with enhanced oil recovery as an ancillary benefit (fifth panel).
- d) In Mission IV (bottom panel), both the land and ocean sinks for CO<sub>2</sub> are enhanced.

Elaborating on the representation of “enhanced oil recovery (EOR)” in the fifth panel, it is worth noting that the current focus of EOR is to minimize the ratio of carbon-in (as purchased CO<sub>2</sub>) to carbon-out (as oil), because there is no economic value for storing CO<sub>2</sub>. In the regime envisioned in Figure A4.3, policies reward CO<sub>2</sub> storage and the carbon-in to carbon-out ratio is substantially greater than unity.

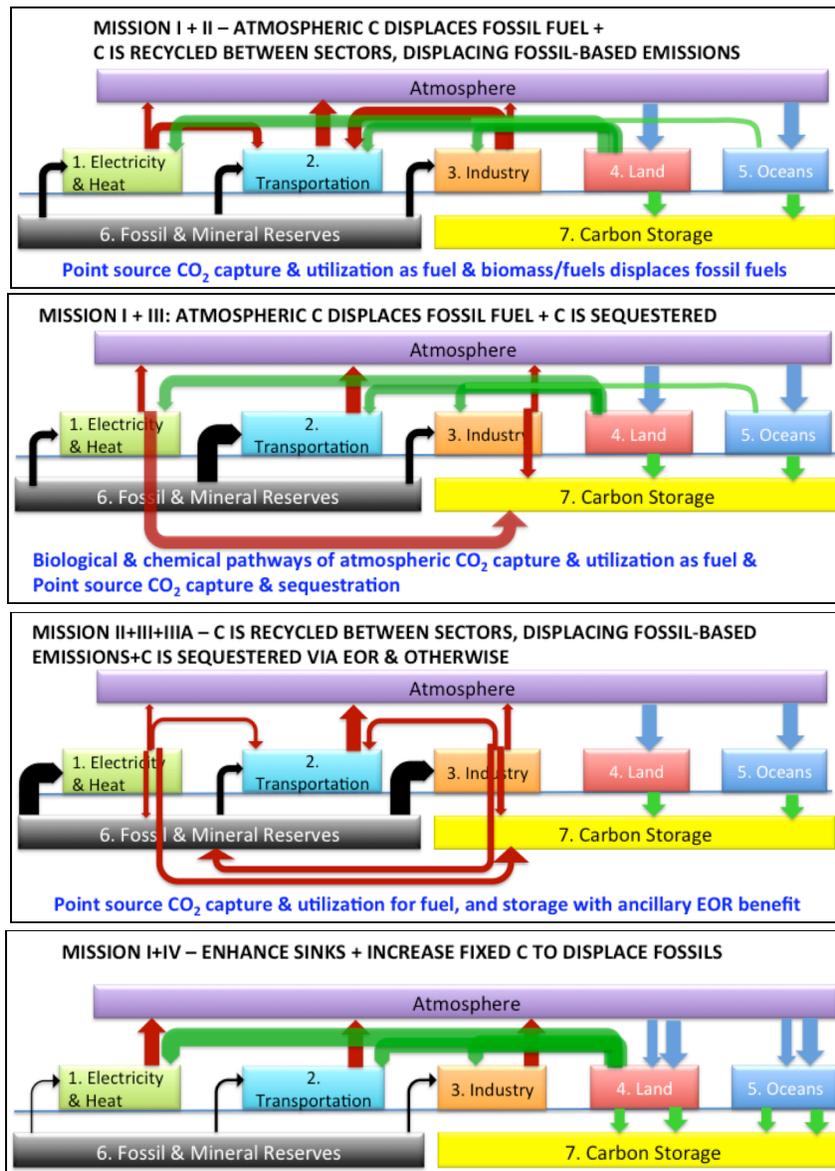
These four Missions can be viewed as building blocks that can be coupled together to form more complex systems of pathways that have the potential to render much greater impact on negative emissions than what can be achieved by individual Missions. Figure A4.4 shows a few of these combinations. Both Missions I+II and Missions I+III use carbon fixed on land and in the oceans to provide carbon-based fuels for the three commercial sectors, thus displacing their fossil fuel use. Mission I+II also uses the carbon emitted from electricity/heat and industry to further displace fossil fuel use in



**Figure A4.3** Carbon pathways between atmosphere, land and oceans involving natural as well as anthropogenic ones that arise from fossil fuel use in electricity and heat, transportation, and industry sectors of our global economy. In addition to the business-as-usual scenario, various missions (I-IV) depict how these pathways could be altered via carbon utilization between sectors or increasing negative emissions and storage.

transportation, while Missions I+III captures the carbon from the electricity/heat and industrial sectors and stores it deep below ground (e.g. in saline aquifers). Note that the process widely known as bioenergy carbon capture and storage (BECCS) is essentially Missions I+III.

As is evident, using the Missions as building blocks, one can develop complex systems of pathways that can have much larger impact on negative emissions than individual



**Figure A4.4** Combinations of various missions can be utilized to amplify carbon utilization between sectors and overall negative emissions.

ones. To achieve the GtCO<sub>2</sub>/yr scale, such combinations may be necessary. It is worth noting that the carbon fluxes between the natural systems - atmosphere, land, and oceans – and commercial systems – electricity/heat, transportation, and industry – have to satisfy the laws of nature, with the commercial system having to satisfy the laws of economics as well. While the laws of nature (thermodynamics, kinetics of phase equilibria, carbon reactions, mass transport, etc.) are universal, the laws of economics are human-designed and vary across the world. These sets of laws invariably introduce non-linearity in the system, which could be potentially ignored at small scale, but would be risky to do so at the GtCO<sub>2</sub>/yr-scale. This makes predictions of the overall system behavior, such as net negative emissions, very difficult.

While our goal is to reduce overall emissions and decarbonize the atmosphere at the GtCO<sub>2</sub>/yr-scale, the choice of individual Missions or combinations of them can be expected to have a wide range of ecological consequences. Nearly all interventions will have impacts on land and soil, water, biota and ecosystems, and albedo. For some proposed interventions, the infiltration of genetically modified organisms may be consequential. Some environmental impacts will be positive and will be seen as co-benefits; others will force trade-offs and may be seen as potential show-stoppers. New scientific understanding is likely to be required in order to provide estimates of central values and uncertainties in each area of environmental concern. In some areas, the appropriate methodology may be risk assessment.

Societal impacts will also require study and response. Issues range from selective impact on vulnerable populations to mainstream societal acceptance, and from legitimization of top-down decision-making to facilitation of broad participation. Policy instruments enabling interventions, both fiscal and regulatory, will require assessment.

It should become abundantly clear that because of the complexity of the system, it is imperative that the modeling of the system, including both natural and human-made pathways for carbon, should be a research effort in itself. Today's integrated assessment models do not capture all the pathways depicted in Figs. A4.3 and A4.4.

This leads to the following Recommendation:

**Systems Modeling:** Given the complexity of both natural and engineering pathways for carbon in our biosphere, intensify research programs that build on and expand today's systems modeling of the global carbon balance that includes carbon mass transport, reactions, phase equilibria and various thermodynamic and kinetic effects for both natural as well as engineered systems. This modeling goes beyond today's integrated assessment models, which do not consider the full impact of all technological pathways in engineered systems at the GtCO<sub>2</sub>/yr scale. Such a tool will be essential to:

- a) Provide a framework to guide our holistic thinking about carbon management.
- b) Model the complex interactions involved in the global carbon balance that could lead to predictions of non-linear systems behavior that cannot be foreseen today.
- c) Develop approaches to systematically study parametric sensitivity and quantify uncertainties of different variables and their collective impact on policy making.
- d) Allow researchers to explore "what if" scenarios and thereby identify individual or combinations of technological pathways, both existing as well as new and disruptive, that would produce large net positive (or negative) GtCO<sub>2</sub>/yr-scale effects on carbon while minimizing the adverse ecological impact. Such an approach could use 0.1 GtCO<sub>2</sub>/yr as a filter to further evaluate the potential for scale-up to 1 GtCO<sub>2</sub>/yr. Furthermore, it could also identify multiplier effects as well as dead ends for various technological pathways that may not be obvious otherwise.
- e) Identify performance and cost targets that would shape a RD&D strategy for these technological pathways.
- f) Develop a roadmap to expedite scale-up of technologies and infrastructure to accelerate negative emissions and CO<sub>2</sub> utilization to the GtCO<sub>2</sub>/yr scale.

Complementary to the research effort in systems modeling, we also recommend:

- g) Emphasize or create an effort for global data collection and analysis to validate the predictions of the models.

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We also recommend that the scientific community should be brought together in a workshop to identify the details of the research program proposed here.

**APPENDIX 5**

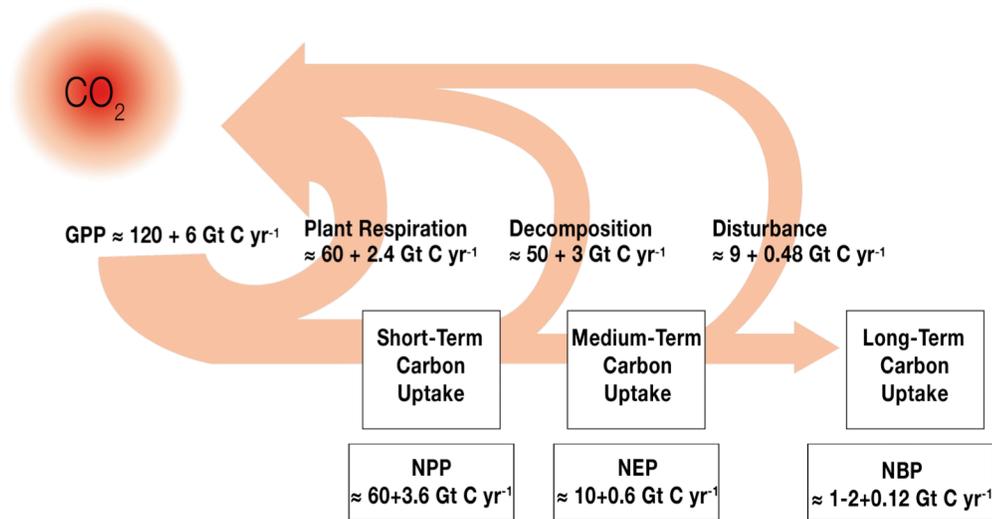
## HARNESSING THE NATURAL BIOLOGICAL CARBON CYCLE

Introduction: Human activities are currently producing ~39 GtCO<sub>2</sub>/yr with about 18 GtCO<sub>2</sub>/yr, or about 2 ppm/yr, accumulating in the atmosphere. The remaining ~21 GtCO<sub>2</sub>/yr is consumed by the ocean and the terrestrial biosphere, demonstrating that the Earth's biological carbon cycle has an enormous CO<sub>2</sub> absorption capacity. Since it is evident that perturbations to the natural biological carbon cycle can result in significant net removal of CO<sub>2</sub> from the atmosphere, are there opportunities to achieve even greater uptake? The terrestrial biosphere is responsible for ~11 GtCO<sub>2</sub>/yr of this uptake and removal of CO<sub>2</sub> from air, which is driven by changes in the nature of the terrestrial carbon sinks and perhaps by the rate of carbon input into those sinks, by the stimulation of C3 photosynthesis by elevated CO<sub>2</sub> concentrations that have risen from 270 ppm to 400 ppm during the 200 years since the beginning of the Industrial Era. Higher atmospheric CO<sub>2</sub> concentrations stimulate C3 photosynthesis because past and current CO<sub>2</sub> concentrations are not saturating substrate levels for the primary C3 plant carboxylase Rubisco (Ribulose-1,5-bisphosphate carboxylase/oxygenase) and because higher CO<sub>2</sub> concentrations competitively suppress the "reverse photosynthesis" oxygenation reaction that Rubisco also catalyzes. Much of the ~11 GtCO<sub>2</sub>/yr uptake by the terrestrial biosphere is attributed to forest regrowth; in particular, the eastern North American forest and secondary tropical forest regrowth. While it has been difficult to resolve CO<sub>2</sub> fertilization of photosynthesis at the global scale, enhancing photosynthesis in other ways in principle has GtCO<sub>2</sub>/yr potential.

Although primary producers in the ocean are responsible for nearly half of biospheric photosynthetic carbon capture, they represent only 0.2% of global primary producer biomass because of a greater than three orders of magnitude faster turnover time of the photosynthetically produced organic matter in the oceans (average residence time of 2-6 days) than in the terrestrial biosphere (average of ~19 years). Because of the rapid turnover of oceanic organic biomass, even large increases in carbon capture rate may not be expected to result in substantial carbon storage through changes in

phytoplankton standing stock, unless the rate of carbon export to greater depths is significantly accelerated over what they are now (Field et al. 1998). By contrast, in terrestrial systems, even modest increases in carbon capture rate could potentially result in substantial carbon storage in plants and soils.

Terrestrial Carbon Cycle: Annual terrestrial net primary productivity (NPP) is estimated at  $\sim 220 \text{ GtCO}_2$  (60 GtC) (see Figure A5.1). Crop NPP contributes  $\sim 30 \text{ GtCO}_2$  (8 GtC) and pasture NPP  $\sim 48 \text{ GtCO}_2$  (13 GtC). There is a range of strategies to improve the photosynthetic efficiency of both C3 and C4 plants (Zhu et al., 2010; Ort et al. 2015) and thereby increase NPP on lands where improved crop or pasture plants replace the extant genotypes. An upper bound on atmospheric  $\text{CO}_2$  concentration reduction that might be achieved by improving photosynthetic efficiency can be visualized by supposing that crop and pasture NPP were increased by 25% through the engineering



**Figure A5.1** Annual Terrestrial Carbon Cycle, expressed in GtC/yr, noting that 1 GtC/yr is about 3.67 GtCO<sub>2</sub>/yr when the carbon is in the form of CO<sub>2</sub>. About 50% of the initial uptake of carbon through photosynthesis [gross primary production (GPP)] is used by plants for growth and maintenance. The remaining carbon is net primary production (NPP), the majority of which is shed as litter and enters the soil, where it decomposes, releasing nutrients to the soil and CO<sub>2</sub> to the atmosphere. The remaining carbon after these emissions is net ecosystem production (NEP), the majority of which is lost to nonrespiratory disturbance processes such as fire, insect damage, and harvest. The remaining carbon is net biome production (NBP) representing just 2 to 3% of the initial uptake of CO<sub>2</sub> from the atmosphere. NBP is the most relevant parameter to consider for decadal or longer carbon storage. About two-thirds of the terrestrial carbon stock is in the rhizosphere. Adapted from *Science* **280**, 1393-1394 (1998).

of plants with higher photosynthetic efficiency.

This example suggests that a 25% improvement in NPP on all crop and pasture lands globally could offset 7% of global anthropogenic carbon emissions. However, the ~10% conversion efficiency of NEP to NBP assumed here is a significant overestimate for annual crop plants, where as much as 50% of the biomass is removed in the food/feed harvest and the majority of the crop residue decomposes quickly. Thus in order to use enhanced crop NPP as a carbon reduction strategy it would need to be coupled with novel strategies to enhance carbon sequestration in the soil and improve the resilience of crop residue with respect to decomposition. Because soil carbon decomposition decays exponentially with depth in the rhizosphere, these would include opportunities to grow deeper roots as well as roots with higher lignin content that would decompose more slowly (Paustian et al. 2015).

*Crops:* Agricultural production has led to a net transfer of terrestrial carbon to the atmosphere. Over the 10,000-year history of agriculture, soil carbon has decreased globally by an estimated 840 GtCO<sub>2</sub> (Lal, 2001). CO<sub>2</sub> emissions associated with U.S. Corn Belt crop production and agricultural lime application were ~26 MtCO<sub>2</sub> for 2004 (West et al. 2010). No-till agriculture is one proven strategy to improve net soil carbon sequestration on croplands. It has been estimated that a change from conventional tillage to no-till agriculture could result in net soil carbon sequestration on U.S. farms as much as 1.2 GtCO<sub>2</sub>/yr (Marland et al. 2003). Bernacchi et al. (2005) estimated that current corn/soybean agriculture in the US releases ~ 26 MtCO<sub>2</sub> annually, with no-till sequestering ~8 MtCO<sub>2</sub> and conventional-till releasing ~34 MtCO<sub>2</sub>. The complete conversion of the U.S. corn/soybean ecosystem to no-till practices could potentially result in ~80 MtCO<sub>2</sub> sequestered annually, representing a net C flux difference of ~ 106 MtCO<sub>2</sub> offsetting 2% of annual US carbon emissions. Based on past soil carbon losses and the availability of land over the next 50 years, physical potential soil carbon sequestration ranges between 110 and 180 GtCO<sub>2</sub> (Lal, 2004).

*Biochar:* Biochar, that is biomass-derived charcoal, used as a soil amendment has been promoted as an option to sequester soil organic carbon and thereby contribute to atmospheric decarbonization. The amendment impact on soil properties, agronomic yield, gaseous emission, and recalcitrance to decomposition varies among different sources with as much as 35 to 85% of biochar C resistant to biological and general chemical degradation far exceeding the stability of raw biomass. There are published estimates that biochar has the potential capacity to sequester multiple GtCO<sub>2</sub> (e.g., Lehmann et al., 2006; Skackley et al. 2009) but these claims are based largely on greenhouse or laboratory studies (Gurwick et al. 2013). There are too few long-term field experiments to substantiate meaningful soil carbon sequestration due to the soil application of biochar and claims of universally beneficial impacts of its application on soil quality and ability to support improved plant growth and yield are also not consistent with available data (Lal, 2015). Both climate mitigation effects and soil quality effects of biochar depend on an array of intricate and interdependent factors for which a great deal of uncertainty exists (Lorenz and Lal, 2014).

*Forests:* Improving NPP in forests as a method to decarbonize the atmosphere may be more promising than for crop and pasture plants due to the much greater portion of the NPP that is captured in slowly decomposing lignocellulose. Globally combined broadleaf and needle leaf forests account for an annual NPP of ~33 GtCO<sub>2</sub> (9 GtC). The restoration of forest on recently deforested land (reforestation) and the restoration of forest on land that has been deforested for >50 years (afforestation) currently have a net uptake of about ~1 GtCO<sub>2</sub>/y (Baumert et al., 2005) even while deforestation is the largest source of land-use-change greenhouse emissions. Significant and sustained removal of CO<sub>2</sub> from the atmosphere by increasing forest NPP would have a large land footprint. For example, removing 3.7 GtCO<sub>2</sub>/yr through tropical afforestation is estimated to require land use change of at least 7 Mha/yr or about 70000 square kilometers per year (Torn, 2013). The amount of carbon that can be removed from the atmosphere through reforestation and afforestation has biologically constrained limits. As a forest matures, the rate of CO<sub>2</sub> uptake is balanced by respiration and the decay of dead organic matter causing the rate of net uptake to decline to zero in the timeframe of 30-

40 years although this depends on forest type and site. By estimating land availability over the next 100 years, afforestation/reforestation may have a global cumulative potential of 380 GtCO<sub>2</sub> (Nilsson and Schopfhauser, 1995), which is roughly nine years of delay at current rates of global emissions.

Water Use Efficiency: Without improvements in water use efficiency (WUE), improvements in NPP may have limited potential. Fortunately, some strategies to improve photosynthetic efficiency would also result in improved WUE because of the very tight relationship between CO<sub>2</sub> uptake and water loss by leaves. For example, any designs that reduce Rubisco oxygenation or the energetic costs of subsequent photorespiration will improve WUE, as would the introduction of bacterial/algal CO<sub>2</sub> concentrating mechanisms (mimicking the higher WUE in C<sub>4</sub> plants). While both C<sub>3</sub> and C<sub>4</sub> plants reduce water loss when grown in elevated CO<sub>2</sub> concentrations by reducing stomatal aperture, C<sub>4</sub> plants appear not to reduce it enough. At 400 ppm atmospheric CO<sub>2</sub> concentrations, the internal CO<sub>2</sub> concentration is ~30% over that needed to saturate photosynthesis, thereby reducing WUE; this opportunity becomes greater as CO<sub>2</sub> concentrations continues to rise. Further reducing stomatal aperture in C<sub>3</sub> plants would reduce photosynthesis because, without the C<sub>4</sub> carbon concentrating mechanism, the internal CO<sub>2</sub> concentration is not saturating for photosynthesis. However, there is a resistance to the internal CO<sub>2</sub> diffusion in C<sub>3</sub> plants between the intercellular airspace and the site of carboxylation by Rubisco in the chloroplast that is as large as the stomatal resistance. Reducing this resistance (often referred to as mesophyll resistance) would increase photosynthesis without any additional loss of water, thereby improving WUE. There are more examples of modifications that could be made that would be expected to both increase photosynthetic and water use efficiency.

Marine Biomass: The use of marine biomass, such as macroalgae, as a biofuel feedstock largely avoids the issue of water availability and WUE as well as concerns of land use competition with crop plants. While macroalgae as a biofuel feedstock is not a negative carbon strategy itself, as a component of a BECCS pipeline it becomes so.

There is already a non-U.S. commercial production of macroalgae, mainly for food products, which is very small<sup>12</sup> when compared with the scale of cultivation needed for macroalgae to be considered a significant contributor to the biomass needed to meet EISA production goals. Replacing 1% of the domestic gasoline supply using macroalgae feedstock would require annual production an order of magnitude larger than current worldwide production and require >10,000 km<sup>2</sup> of ocean surface (Roesijadi et al., 2010). The marine biomass resource potential for the United States is seemingly very high based on the surface area of the U.S. coastal waters and known rates of macroalgae production in other parts of the world but production of biofuel from seaweed is economically, energetically and technically quite daunting at scale. That said, the measured biomass yield of macroalgae per unit area can be quite high. For example, brown seaweeds grown 'under cultured conditions' can attain yields of ~13.1 kg dry weight m<sup>-2</sup> yr<sup>-1</sup> (Rujkumar et al. 2014). While it is frequently stated that macroalgae have higher photosynthetic solar energy conversion efficiency than terrestrial C4 plants this is not experimentally well supported and difficult to explain mechanistically. In order for macroalgae to fulfill its seemly high potential as a biofuel feedstock, breakthrough improvements are needed in each of the process operations of algal-derived fuel production: cultivation (including seedling production), harvesting, post-harvest treatments including water removal, preservation, storage, and energy extraction (Milledge and Harvey, 2016).

In conclusion, there is no doubt that enhancing NPP as a strategy to decarbonize the atmosphere has significant potential and capacity; in fact, it is difficult imagine how atmospheric CO<sub>2</sub> levels can be maintained within acceptable boundaries without greater net global NPP playing a major role. In all cases the scale is huge in terms of land, water and plant nutritional requirements, putting increased carbon sequestration on a collision course with society's needs to produce more food, feed, and fiber, unless new technologies can be developed and implemented or the potential of marine biomass can be realized. It is further important to recognize that CO<sub>2</sub> removed from the atmosphere

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<sup>12</sup> The global production is roughly 8 million tonnes per year (<http://www.fao.org/docrep/006/y4765e/y4765e04.htm#fnB1>).

and sequestered in organic matter is intrinsically labile. For example to implement enhanced photosynthesis as an effective strategy to decarbonize the atmosphere, fastidious management of the stored carbon is required. For example, mature forests that are no longer net CO<sub>2</sub> consumers must be maintained and no-till acreage must forever stay no-till long after soil carbon is saturated, unless novel technologies are devised to store and prevent the decomposition of the organic carbon.

Considering intervention in the biology of the global carbon cycle to achieve “negative CO<sub>2</sub>” reveals critical gaps in our current knowledge and in technology that are research *imperatives*. For example:

- Converting crop lands from net CO<sub>2</sub> producers to net carbon sinks requires a much improved understanding of the biology and chemistry of resilient soil carbon.
- Realizing macroalgae as a GtCO<sub>2</sub>/yr scale requires developing process operations for each step of algal-derived fuel production.
- While the potential impact of strategies to improve photosynthesis in plants is clear, the molecular technology to redesign photosynthesis (e.g., importing in plants carbon concentration mechanisms that operate in photosynthetic bacteria and algae) is often lacking.

Based on this background, the Task Force feels that this topic deserves increased RD&D attention to explore and develop the following capabilities:

- a) Increase the photosynthetic efficiency<sup>13</sup> and optimize crops for food, bioenergy, feed, and fiber, as well as trees used for bioenergy, reforestation and afforestation, with no marginal increase in resource inputs, such as fresh water, fertilizers, and pesticides, and preferably with reductions in each of these.

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<sup>13</sup> It should be noted that among the most innovative and potentially high-impact strategies to improve photosynthesis in plants is to import carbon concentration mechanisms that operate in photosynthetic bacteria and algae. The opportunity is clear but the molecular technology to import these complex components is lacking, as is a full understanding of the biology of their assembly.

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- b) Rigorously evaluate the benefits and limitations of marine macroalgae as a bioenergy feedstock for both land-based energy (e.g., for BECCS) as well as for liquid transportation fuels.
- c) Identify approaches to reduce decomposition of soil organic carbon and N<sub>2</sub>O emission impact by taking into account the biology and chemistry of soil carbon decay. Examples include creating roots that go deeper in the rhizosphere with higher lignin content.
- d) Optimize crops and management technology that stabilize organic carbon over longer time frames, including accelerating the transition to no-till agriculture, sustaining no-till land after the transition is made, and extending the period in which forests are net CO<sub>2</sub> sinks.
- e) Because of the complexity of the biosphere, intensify research in understanding the ecological impact of harnessing the natural biological carbon cycle, including using systems modeling (**Appendix 4**) to understand the net global carbon impact.

It is important to point out that BECCS has been highlighted by many reports as one of the key strategies for negative emissions. The Task Force agrees with that assessment. But, the Task Force notes that the net positive impact of BECCS can be significantly increased through RD&D proposed in Recommendation 2.

While intervening in the natural biological carbon cycle to decarbonize the atmosphere has the potential for GtCO<sub>2</sub>/yr scale impact, the Task Force cautions that this must be undertaken thoughtfully and carefully because the consequences, intended and unintended, of such an endeavor can be large and unpredictable.

### References

- Baumert, K., T. Herzog, and J. Pershing. 2005. Navigating the Numbers: Greenhouse Gases and International Climate Change Agreements. Washington, DC: World Resources Institute.
- Bernacchi, C. J., S. E. Hollinger, and T. Meyers. 2005. The conversion of the corn/soybean ecosystem to no-till agriculture may result in a carbon sink. *Global Change Biology* **11**, pp. 1867–1872.

- Field, C. B., M. J. Behrenfeld, J. T. Randerson, and P. Falkowski. 1998. Primary production of the biosphere: Integrating terrestrial and oceanic components. *Science* **281**, pp. 237-240.
- Lal, R. 2001. Soil degradation by erosion. *Land Degradation & Development* **12**, pp. 519-539.
- Lal, R. 2004. Soil carbon sequestration impacts on global climate change and food security. *Science* **304**, pp. 1623-1627.
- Lal, R. 2015. Biochar and soil carbon sequestration. In *Agricultural and Environmental Applications of Biochar: Advances and Barriers*. ed. M. Guo, Z. He and S. M. Uchimiya. Madison, WI, *Soil Science Society of America, Inc.*, pp.175-198
- Lehmann, J., J. Gaunt, and M. Rondon. 2006. Bio-char sequestration in terrestrial ecosystems—A review. *Mitig. Adapt. Strategies Glob. Change* **11**, pp. 395–419.
- Lorenz, K., and R. Lal. 2014. Biochar application to soil for climate change mitigation by soil organic carbon sequestration. *J. Plant Nutr. Soil Sci.* **177**, pp. 651–670.
- Milledge, J.J., P.J.Harvey 2016. Potential process ‘hurdles’ in the use of macroalgae as feedstock for biofuel production in the British Isles. *Journal of Chemical Technology & Biotechnology* DOI 10.1002/jctb.5003
- Marland, G., T. O. West, B. Schlamadinger, and L. Canella. 2003. Managing soil organic carbon in agriculture: The net effect on greenhouse gas emissions. *Tellus Series B: Chemical and Physical Meteorology* **55**, pp. 613-621.
- Nilsson, S., and W. Schopfhauser. 1995. The carbon-sequestration potential of a global afforestation program. *Climatic Change* **30**, pp. 267-293.
- Ort, D.R., Merchant, S.S., Alric, J., Barkan, A., Blankenship, R.E., Bock, R., Croce, R., Hanson, M.R., Hibberd, J.M., Long, S.P., Moore, T.A., Moroney J.V., Niyogi, K.K., Parry, M.A.J., Peralta-Yahya, P.P., Prince, R.C., Redding, K.E., Spalding, M.H., van Wijk, K.J., Vermaas, W.F.J., von Caemmerer, S., Weber, A.P.M., Yeates, T.O., Yuan, J.S., and Zhu, X. 2015. Can photosynthesis be redesigned to sustainably meet global food and bioenergy demand. *Proceeding of National Academy of Sciences USA*. **112**, pp. 8529-8536.
- Paustian, K., Campbell, N., Dorich, C., Marx, E., and Swan, A. 2015. Assessment of potential greenhouse gas mitigation from changes to crop root mass and architecture. *Report to ARPA-E. Accessible at:* (<https://arpa-e-foa.energy.gov/Default.aspx#Foald40aa63a7-689b-4307-90b2-c1b98a2148a3>)
- Rajkumar R., Z. Yaakob, M.S. Takriff, 2014. Potential of the micro and macro algae for biofuel production: a brief review. *BioResources* **9**, pp. 1606–1633.
- Roesijadi, G., A.E. Copping, M.H. Huesemann, J. Forster, J.R. Benemann 2008. Techno-Economic Feasibility Analysis of Offshore Seaweed Farming for Bioenergy and Biobased Products, Battelle Pacific Northwest Division Report Number PNWD-3931.
- Roesijadi, G., S.B. Jones, L.J. Snowden-Swan, Y. Zhu 2010. Macroalgae as a biomass feedstock: A preliminary analysis. <https://www.researchgate.net/publication/255221448>
- Shackley, S., S. Sohi, S. Haszeldine, D. Manning and O. Masek. 2009. Biochar: reducing and removing CO<sub>2</sub> while improving soils: A significant and sustainable response to climate change? Royal Society Geo-engineering Climate Enquiry. <http://www.geosciences.ed.ac.uk/homes/sshackle/WP2.pdf>

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- Torn, M. S., Kleber, M., Zavaleta, E. S., Zhu, B., Field, C. B., and Trumbore, S. E. 2013. A dual isotope approach to isolate carbon pools of different turnover times. *Biogeosciences* **10**, pp. 8067-8081.
- West et al. 2010. Cropland fluxes in the United States: increasing geospatial resolution of inventory-based carbon accounting. *Ecological Applications* **20**, pp. 1074-1086.
- Zhu, X-G., Long, S.P., and Ort D.R. 2010. Improving photosynthetic efficiency for greater yield. *Annual Reviews of Plant Biology* **61**, pp. 235-261.

**APPENDIX 6**SYNTHETIC TRANSFORMATIONS OF CO<sub>2</sub>

Carbon dioxide is at the lowest free energy state of carbon and any transformation of CO<sub>2</sub> into something of value generally requires an input of energy such that the carbon is chemically reduced.<sup>14</sup> For example, if CO<sub>2</sub> is transformed into hydrocarbon fuel, the amount of energy needed is at the very least the energy that can be obtained by combusting that fuel. The necessary reducing equivalents must come from sources that are carbon neutral, or preferably carbon free. Figure A6.1 shows the potential pathways for chemical transformation of CO<sub>2</sub>, either by direct reduction of CO<sub>2</sub> or via production of carbon-free/neutral H<sub>2</sub> first and then using H<sub>2</sub> to reduce CO<sub>2</sub> and form various hydrocarbons and alcohols.

To ensure that the chemical and fuels made from CO<sub>2</sub> are market competitive and can achieve the GtCO<sub>2</sub>/yr scale, it is important to first ensure that the feedstock (CO<sub>2</sub>, water, energy) have the right scale and economics. We will then look at the various pathways needed to transform CO<sub>2</sub> into chemical and fuels.

GigaTonne Scale Applications: If we are to explore opportunities at the GtCO<sub>2</sub>/yr scale, what are the applications that match this scale? Let us consider plastics and fuel. In 2014, the annual global production of plastics was 311MT (Plastics2015). Roughly 50 percent of plastics are made of polyethylene or polypropylene, for which the carbon percentage by weight is about 85 percent. For the other dominant plastics such as PVC and PTFE, the carbon percentage by weight is roughly 40 and 24 percent, respectively. Using an approximate production-averaged weight percentage of carbon as 70 percent, the carbon content by weight of 311MT of plastic is about 218MtC. If the source of all the carbon were CO<sub>2</sub>, then it would require about 0.8 GtCO<sub>2</sub> per year. This does not

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<sup>14</sup> The reaction of CO<sub>2</sub>+H<sub>2</sub>O → H<sup>+</sup> + HCO<sub>3</sub><sup>-</sup> does not require any energy input. The bicarbonate anion (HCO<sub>3</sub><sup>-</sup>) can react with cations such as Na<sup>+</sup> or Ca<sup>++</sup> to form bicarbonate or carbonate salts. However, the remaining proton (H<sup>+</sup>), reduces pH, as is found when CO<sub>2</sub> reacts with ocean water. Hence, scalable approaches to form bicarbonate or carbonate materials require large supplies of alkaline salts to neutralize the acidity. While alkaline rocks such as basalt and serpentine do exist, getting the alkaline materials to mix with water and form salts requires significant infrastructure and materials at scale. This has well covered by McNutt et al., Climate Intervention: Carbon Dioxide Removal and Reliable Sequestration, National Research Council Report, The National Academies Press (2015).

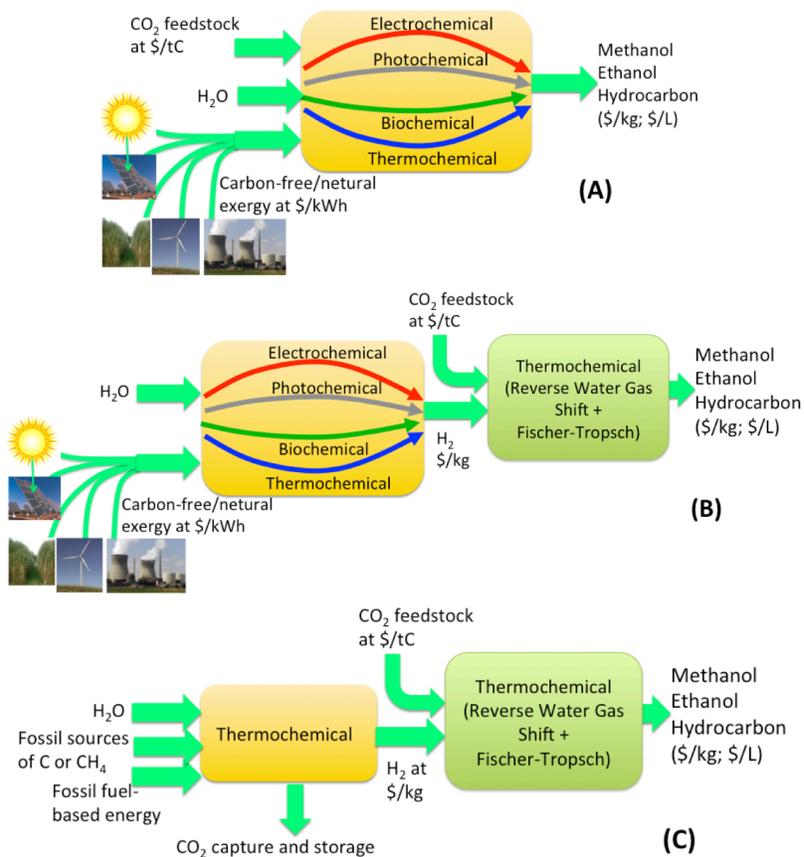
account for the displacement of fossil fuels required to make these plastics, which includes both the carbon and the energy needed to do so. Since the wholesale price of plastics is roughly \$2/kg (Kantchev & Ng, 2015) the value of carbon in plastics equates to about \$2.9/kg-C, or \$0.78/kg-CO<sub>2</sub> or \$780/tCO<sub>2</sub>. Such a high price of CO<sub>2</sub> offers sufficient headroom for the CO<sub>2</sub> cost to be lower, allowing manufacture of high-value products such as plastics to offer a pathway to cost-effectively produce lower-value products such as fuels that already have the GtCO<sub>2</sub>/yr scale. By 2030, the annual global plastic production is expected to rise to 700 MT (Plastics2030), which would require roughly 490 MtC or about 1.8 GtCO<sub>2</sub>. The only other application that really matches the scale is fuels. In 2015, the US transportation sector produced 1.8 GtCO<sub>2</sub> (or 0.5 GtC), suggesting that replacement of a large fraction of transportation fuels could have GtCO<sub>2</sub>/yr scale impact. The production of liquid fuels from inorganic carbon requires both a source of carbon and a source of energy. To be carbon neutral, that carbon should be derived from a post-combustion source, and the reducing equivalents must themselves not release geologic carbon as CO<sub>2</sub>.

Carbon Dioxide as a Feedstock: Carbon can be captured from concentrated waste streams or from dilute sources,<sup>15</sup> so-called direct air capture. Annually, the US produced 3.2 Gt of concentrated CO<sub>2</sub> from 8,000 point sources; two-thirds of this CO<sub>2</sub> was from 1,500 power plants. Carbon can be captured from point sources through post-combustion, pre-combustion, or oxyfuel processes. The cost per ton of avoided CO<sub>2</sub> for these processes range from \$60-70/tCO<sub>2</sub> for coal-fired processes and \$90-130/tCO<sub>2</sub> for gas-fired processes (see **Appendix 8**). As these sources are eliminated, dilute capture from air will become increasingly important. Capture of CO<sub>2</sub> from the atmosphere poses significant technical and environmental challenges, with recent cost estimates (Socolow et al, 2011) on the order of \$600/tCO<sub>2</sub>, although research efforts are underway to reduce the cost.

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<sup>15</sup> We note parenthetically that to satisfy our definition of negative CO<sub>2</sub> production, this approach requires as an input anthropogenic CO<sub>2</sub> that would otherwise have been released to the atmosphere, from the burning of fossil fuels and industrial processes such as steel and cement/concrete production.

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**Fig. A6.1** Chemical transformation of CO<sub>2</sub> involves CO<sub>2</sub> as a feedstock at \$/tC cost, water, and carbon-free/neutral energy at \$/kWh. (A) CO<sub>2</sub> could be directly transformed via electrochemical, photochemical, biochemical or thermochemical pathways (or a combination of pathways) to produce hydrocarbons or alcohols at market competitive costs (e.g., \$2 per gallon of gasoline equivalent). (B) Alternatively, carbon-free/neutral energy could be used to split water to produce H<sub>2</sub> and O<sub>2</sub>, where H<sub>2</sub> can be used in well-known thermochemical pathways (e.g., reverse water gas shift plus Fischer-Tropsch) to produce various hydrocarbons and alcohols. The infrastructure for the latter at the megatonne and potentially gigatonne scale is well known, but the pressure and heat for the latter would need to be supplied from a carbon-neutral/free source. (C) Fossil-based energy can be used to react water with coal and/or natural gas to produce H<sub>2</sub>, which can be made carbon-free by capturing and storing the CO<sub>2</sub> from two sources - the steam reforming reactions themselves and from fossil fuels burned to provide the energy for the endothermic reactions involved steam reforming. H<sub>2</sub> can be used in well-known thermochemical pathways (e.g., reverse water gas shift plus Fischer-Tropsch) to produce various hydrocarbons and alcohols, subject to the need for carbon-neutral/free pressure and heat required for these reactions

Perhaps the most plausible approach to direct air capture involves photosynthesis, a process that both fixes atmospheric carbon and captures reducing equivalents in the form of reduced carbon. The joint USDA/DOE Billion Ton study suggested that the United States can produce 1.3B tons/year of dry biomass without impacting the country's ability to produce sufficient food, or on the order of 0.7 GtC/year, an amount

sufficient to produce all US liquid transportation fuels. Biomass costs range from \$30 to over \$200/dry ton, or \$60 to over \$400/ton C. Several important challenges regarding the implementation of these strategies remain, including addressing chronic water shortages.

Although reduction of carbon capture cost is necessary for CO<sub>2</sub> utilization, it may not be the dominant one. For example, a \$40/tCO<sub>2</sub> price adds \$0.37 to the production cost of a gallon of gasoline<sup>16</sup>. Figure A6.1 shows that the additional cost in the process is the cost of carbon-free/neutral energy.

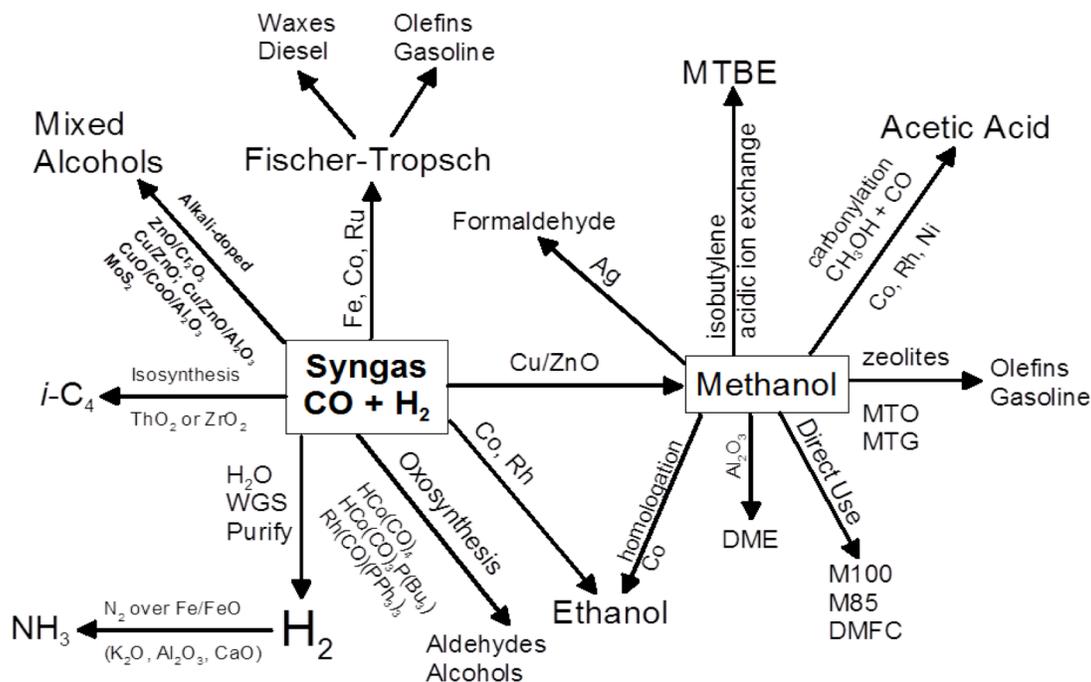
Case for Hydrogen and the Cost of Energy: Liquid fuels serve as energy storage media, and it is thus not surprising that energy costs represent the largest single contributor to the costs of fuel. Significantly, CO<sub>2</sub> costs are a relatively minor cost driver, as discussed above. What should be the cost of energy to make fuels from CO<sub>2</sub> cost competitive? We will use H<sub>2</sub>, one key to transforming CO<sub>2</sub> to fuels, as an example to highlight the cost of energy.

Currently, H<sub>2</sub> is a \$100B per year global industry with about 50 million tons of H<sub>2</sub> produced annually, with the US producing roughly 10-12 million tons. About 40 percent of the H<sub>2</sub> is used for ammonia production that is used to make artificial fertilizers, and 20 percent for hydrogenation in petrochemical refineries. The total GHG footprint of the chemical industry (IEA 2013) is 1.2 GtCO<sub>2</sub>/yr. Decarbonizing this industry by producing carbon-free/neutral H<sub>2</sub> is itself a worthy goal, with the added benefit of decoupling from the global oil market with its accompanying price fluctuations and market inefficiencies. But there is a significant added benefit because of the versatility that H<sub>2</sub> offers:

a) the chemical industry infrastructure already exists to use H<sub>2</sub> to reduce CO<sub>2</sub> and form CO via the reverse water gas shift reaction (an endothermic reaction with an enthalpy of 41 kJ/mol or 5.75 kWh/kg-H<sub>2</sub>), and then to use various ratios of CO and

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<sup>16</sup> A useful way to remember the value of carbon in gasoline is that a CO<sub>2</sub> price of \$1/tCO<sub>2</sub> will increase the cost of gasoline by approximately 1 cent per gallon of gasoline equivalent.



**Figure A6.2:** Known and widely used catalytic pathways to produce chemicals and fuels from a mixture of CO and H<sub>2</sub>.

H<sub>2</sub> to form a variety of chemical and fuels (see Fig. A6.2). Hence, low-cost, carbon-free/neutral H<sub>2</sub> production could be one of the essential steps in CO<sub>2</sub> utilization.

- b) the chemical industry infrastructure also exists to combine H<sub>2</sub> and N<sub>2</sub> to form ammonia (Haber-Bosch process), which is the precursor for fertilizers. Although not the focus of the current report, the Haber-Bosch process is also very energy-intensive and could benefit from decarbonization as well.

One key bottleneck in transforming CO<sub>2</sub> to chemicals and fuels is carbon-free or carbon-neutral hydrogen production. This can be achieved by:

- steam reforming of natural gas and coal combined with carbon capture and storage
- splitting water into H<sub>2</sub> and O<sub>2</sub>.

Because the technology for carbon capture is discussed in **Appendix 8**, here we focus on (b), which requires RD&D.

The water splitting reaction  $\text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2}\text{O}_2$  is highly endothermic, with an enthalpy of 286 kJ/mol or roughly 40 kWh/kg- $\text{H}_2$ . Hence, to produce  $\text{H}_2$  at \$2/kg- $\text{H}_2$ <sup>17</sup>, the cost of carbon-free/neutral exergy<sup>18</sup> must be less than 5 cents/kWh at the thermodynamic limit. With this as the upper bound, the inclusion of kinetics and other losses suggest that in reality, the cost of carbon-free/neutral exergy ought to be less than 3 cents/kWh, regardless of which pathway is adopted in Fig. A6.1. While the target for the exergy cost is based on water splitting reactions, it will not be fundamentally different for direct  $\text{CO}_2$  reduction since most of the energy<sup>19</sup> is embedded in  $\text{H}_2$  (Fig. A6.1 Top). Hence, part of the RD&D effort for  $\text{CO}_2$  chemical transformation should be focused on reducing the cost of carbon-free/neutral energy, of both electricity and heat.

Currently, the lowest unsubsidized levelized cost of utility-scale wind electricity is about 3 cents/kWh whereas that for solar is about 4 cents/kWh (Liebreich, 2016). The global average is roughly 5 and 7-8 cents/kWh, respectively. But these are intermittent sources, which suggests that if wind and solar were the only energy source, it would lead to less than 50 percent capacity utilization of any  $\text{CO}_2$  chemical transformation plant. On the other hand, if there are  $\text{CO}_2$  transformation plants that can utilize and track the intermittency in wind and solar, it could provide value in balancing the electricity grid. With the exception of solar thermal, the advantage of thermal energy sources is that they are not intermittent, leading to much higher capacity utilization. Furthermore, heat can be cheaper than electricity as long as it is of high exergy (high-temperature heat). Currently, the cost of nuclear electricity is about 9-10 cents/kWh, and therefore not within the range required for cost-competitive  $\text{CO}_2$  utilization. However, because heat-to-electricity conversion efficiency of nuclear plants is about 30-35 percent, the cost of nuclear heat is about 3 cents/kWh, and therefore within the

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<sup>17</sup> Note that \$2/kg- $\text{H}_2$  is roughly equivalent to \$2 per gallon of gasoline equivalent, and hence relevant for cost-competitive fuel production.

<sup>18</sup> When thermal energy is used, there is a significant difference between high and low-temperature heat. What is important is the ability to do work, in this case chemical work to split water, which is defined in the form of exergy. In the case of electricity, the energy is equal to the exergy since it is in the form of work.

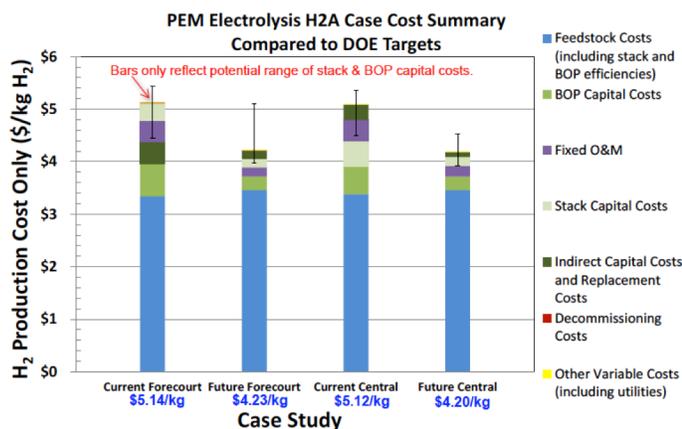
<sup>19</sup> How much energy is required to produce sufficient  $\text{H}_2$  from water splitting to reduce 1 Gt $\text{CO}_2$ /yr? Assuming we need 3 moles of  $\text{H}_2$  for each mole of  $\text{CO}_2$  to form hydrocarbons, then 1 Gt $\text{CO}_2$ /yr would require 6/44 or 0.14 Gt $\text{H}_2$ /yr. Since the water splitting reaction has an enthalpy of 40 kWh/kg- $\text{H}_2$ , 0.14 Gt $\text{H}_2$ /yr would require at least 5600 TWh/yr, which is roughly 19 Quads of energy. Note that the US uses roughly 100 Quads of primary energy. Also as a comparison, the total electricity generation in the US in 2014 was 4093 TWh, out of which 1340 TWh came from carbon-free electricity sources (nuclear, wind, solar, hydroelectric).

target range as long as it is of high exergy<sup>20</sup>. Finally, biomass costs are typically \$30-200/dry ton and has a calorific value of about 7000 BTU/lb or 4.5 kWh/kg-biomass. Hence, the cost of carbon-neutral heat from burning biomass would range from 0.7-4.4 cents/kWh, which is within the range required. Research ought to be focused on solar thermal heat generators with thermal storage at a cost of 2.5-3 cents/kWh.

Pathways for CO<sub>2</sub> Transformations: As shown in Fig. A6.1, there are four different pathways for CO<sub>2</sub> transformations.

*Electrochemical:* Two fundamental processes are required to convert CO<sub>2</sub> to a liquid fuel: reduction of carbon at its +4 oxidation state to zero, and the formation of carbon-carbon bonds, assuming the aim is transportation fuels that are liquids at STP. The reduction of CO<sub>2</sub> requires large energy inputs. There exist chemical and biochemical approaches to both steps; both approaches are in early stages of development and will require scientific breakthroughs, followed by scale-up and infrastructure build-out.

Processes for the electrochemical reduction of CO<sub>2</sub> to CO, formate, and methanol exist, but current catalysts still require significant overpotentials at meaningful current densities (> 20 mA/cm<sup>2</sup>), resulting in low efficiencies; excessive overpotentials also produce complex product mixtures. Electrochemical reduction of CO<sub>2</sub> to



**Fig. A6.3** Cost of H<sub>2</sub> production using PEM electrolyzers. The electricity price is assumed to be 6-7 cents/kWh. With state-of-the-art catalysts, the enthalpy is about 55 kWh/kg-H<sub>2</sub>. Hence, the energy cost is roughly \$3.30/kg-H<sub>2</sub>. The remaining costs are balance of plant capital costs, O&M, etc., which today is roughly \$2/kg-H<sub>2</sub>. This ought to reduce to < \$1/kg-H<sub>2</sub>. Because electrolyzers are modular, there are marginal economies of scale between forecourt (1500 kg-H<sub>2</sub>/day) or central (50,000 kg-H<sub>2</sub>/day) plants (DOE Report, 2014)

<sup>20</sup> If nuclear heat,  $Q$ , is generated at say 600 °C ( $T_h = 873$  K) with the ambient at  $T_o = 300$  K, then exergy  $B = Q(1 - T_o/T_h)$  or 0.66 $Q$ . Hence, if the cost of  $Q$  is 3 cents of kWh of energy, the cost of  $B$  will be  $3/0.66 = 4.5$  cents kWh of exergy.

methane is known to occur, e.g., at Cu electrodes but the real challenge is C-C coupling to make energy-dense fuels. No metal electrodes are capable yet of selective, efficient CO<sub>2</sub> reduction to liquids. Discovery of cheap, robust metal alloys exhibiting fast rates (low overpotentials) that preferentially reduce CO<sub>2</sub> rather than water to liquid fuels or fuel precursors (that can be converted as discussed above) is the game-changer that is required. Product mixtures, as long as they are energy-dense, non-corrosive, and hit the sweet spot of chain length, will be acceptable as drop-in fuels. However, cell design, relatively unimportant at research scales, will be extraordinarily important in consideration of production scales of any electrochemical process to produce fuels of the magnitude required.

Since electrocatalytic reduction of CO<sub>2</sub> to make carbon-based products (e.g., fuels) with high specificity is very challenging, as Fig. A6.1B suggests, it may be easier to split water and produce hydrogen, and then use well-known approaches to react CO<sub>2</sub> and H<sub>2</sub> to make carbon-based products. Electrolytic hydrogen can be synthesized via alkaline, polymer electrolyte membrane (PEM) or solid-oxide electrolyzers. Current baseline costs for hydrogen production from these approaches are \$5.20/kg, \$5.16/kg and \$4.95/kg, respectively, at an electricity cost of \$62.40/MWh. What is the breakdown of these costs? Figure A6.3 shows the data for PEM electrolyzers. While the thermodynamic limit for water splitting is 40 kWh/kg-H<sub>2</sub>, the best performing catalysts offer an enthalpy of 55 kWh/kg-H<sub>2</sub>. Hence, with an electricity cost at 6 cents/kWh, the energy cost itself is about \$3.30/kg-H<sub>2</sub>. Furthermore, the levelized cost of balance of plant and remaining costs for electrolyzers is roughly \$2/kg-H<sub>2</sub>, making the total cost \$5.30/kg-H<sub>2</sub>. Research is needed in the following areas:

- Identify catalysts to lower the overpotentials (voltage efficiency of within 75% of the thermodynamic limit<sup>21</sup>) to below 50 kWh/kg-H<sub>2</sub> at high reaction rates (1-2 A/cm<sup>2</sup>). The key bottleneck is the catalyst for the oxygen evolution reaction (OER), a complicated reaction involving electron transfer, proton transfer, and O-O bond

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<sup>21</sup> For example, if the equilibrium potential required for water splitting is 1.23V, then 75% voltage efficiency would mean an operating voltage of 1.64V.

formation. At least four different mechanisms have been proposed for the OER, complicating catalyst design. Many transition metal oxides or other ionic transition metal catalysts (e.g., phosphates) have been touted for OER, but in fact none meet requirements. While Pt can be used for OER, its cost is prohibitive for scale up. Metal oxyhydroxides, most commonly known as battery materials, are the latest to offer some promise. Basic understanding of the mechanisms by which water loses electrons and protons and ultimately forms O-O bonds is needed to help guide materials discovery.

- Create systems architecture and designs to reduce the non-energy costs to < \$1/kg-H<sub>2</sub>.

Finally, infrastructure for electricity production required to produce hydrogen at the requisite scales is lacking. Thus, for example, production of sufficient hydrogen to make all US transportation fuels through a Fischer-Tropsch (FT) approach would require three times the current nameplate capacity of the entire US electricity generation fleet, even assuming an overpotential of only 25%.

*Photochemical:* Photochemical or photoelectrochemical approaches offer the very significant advantage of direct use of photons, as opposed to initial conversion to electricity. Coupling effectively the phenomena that occur in solar cells with electrochemistry in one material, a photoelectrocatalyst, sounds attractive because one does not suffer efficiency losses necessitated by coupling separate devices together. In reality, requiring all the phenomena to work in concert in the same material requires that all properties must be optimized at once – a very tall order. These properties include the band edge positions (the conduction band edge for reduction and the valence band edge for oxidation), the electron-hole pair lifetime, charge carrier mobility, and finally surface kinetics, include rates of electron and proton transfer and chemical bond formation/breaking. If all phenomena take place in the same material, one must also match fluxes of photons and electrons with reaction rates. Not surprisingly then, this is an area still very much in the basic research phase. The most promising material

systems yet are three different compound semiconductors (GaP, CdTe, CuInS<sub>2</sub>) in the presence of an aromatic amine co-catalyst in acidified water, all of which have been reported to photoelectrochemically reduce CO<sub>2</sub> selectively to a liquid fuel (precursor), namely methanol, at *underpotentials* (Barton et al., 2008; Jeon et al., 2014, Yuan et al., 2013). Although highly selective, none of these systems is particularly active, with very low yields observed. Understanding the complex chemistry and physics of all the phenomena involved here is an active area of basic research that should continue.

In addition to the infrastructure issues outlined above, additional key framing questions in these areas include:

- Effective catalysts and photoactive charge-transport materials based on abundant non-toxic elements are required to facilitate the requisite conversions in high yield and purity.
- Catalytic processes scale as catalyst area. Volumetric approaches that scale as reactor volume are required.

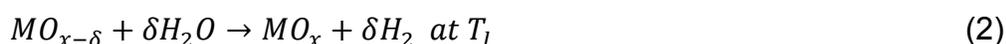
*Biochemical:* Biological approaches offer the potential to both catalyze CO<sub>2</sub> reduction and to form carbon-carbon bonds. An extraordinarily large number of organisms occupy ecological niches where they have access to neither sunlight or reduced carbon; such autotrophs must assimilate energy through other means, including hydrogen, reduced metal ions, nitrogen or, perhaps, electricity. The use of such organisms to convert inorganic carbon and low-cost reducing equivalents could offer an important opportunity to produce both chemicals and fuels. This was first explored through the ARPA-E program called Electrofuels (ARPA, 2010), but much more research is needed to further investigate this area. Critical research objectives include:

- To understand the mechanisms and to measure rates of these processes to determine if they would even be practical to consider, and then to determine how to optimize them.
- To gain a better understanding of the autotrophic microbiome, including the behavior of symbiotic and commensal communities, is required.

- To develop reactor designs suitable for large-scale production with autotrophic organisms is required.

*Thermochemical:* Thermochemical approaches are particularly attractive since today's chemical industry at large scale is predominantly<sup>22</sup> thermochemical. Furthermore, as pointed out earlier, carbon-free/neutral heat is generally less expensive than electricity and is non-intermittent, with the exception of high-temperature solar-thermal without any thermal storage. Hence, CO<sub>2</sub> transformations at the GtCO<sub>2</sub>/yr scale can be conceived if the redox reactions are infrastructure compatible (Stechel and Miller, 2013).

Thermochemical redox reactions have been explored for many decades. Much of the work has focused on using metal oxides based on the two-step reactions



where  $M$  is a metal,  $T_h$  is the high temperature for the O<sub>2</sub> evolution reaction, and  $T_l$  is the lower temperature for the H<sub>2</sub> evolution reaction (or CO<sub>2</sub> to CO reduction reaction). This is essentially a heat engine, which absorbs heat at high temperature, rejects heat at low temperature and produces work in the form of chemically stored energy. The most well-studied systems use ferrites or CeO<sub>2</sub> (Scheffe & Steinfeld, 2014; Agrafiotis et al., 2015). Ferrites can work at lower temperatures than ceria but ceria exhibits much faster bond-breaking rates. Furthermore, ceria's  $T_h > 1500$  °C whereas  $T_l \sim 600-700$  °C. The fact that ceria requires  $T_h > 1500$  °C to achieve appreciable kinetics makes it incompatible with today's chemical industry. Research is needed to get deeper understanding of the enthalpic and entropic driving forces for the two-step redox reactions and thereby identify materials that can operate at temperatures below or about 1000 °C and yet have the appropriate kinetics, as well as oxygen and hydrogen producing capacities. A thermodynamic framework underlying equations (1) and (2) suggests that the entropy change,  $\Delta S$ , of the oxides must be higher than 10 cal/(0.5 mol O<sub>2</sub>)-K (Meredig and Wolverton, 2009) during the reduction process (eqn. 1). However,

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<sup>22</sup> With the exception of aluminum manufacturing and chlorine synthesis, which are based on electrochemical redox reactions.

## DRAFT

for most oxides,  $\Delta S < 0$ . We need research to design materials for which  $\Delta S > 10$  cal/(0.5 mol O<sub>2</sub>)-K, perhaps through the use of phase transitions or via other means, which have remained largely unexplored.

Based on the above discussions, it is necessary create a coherent RD&D program to:

- a) Reduce the cost of delivered carbon-free/neutral exergy (electricity and high-temperature heat) with a target range below 3 cents/kWh.
- b) Focus on fundamentals of electrocatalysis and photoelectrocatalysis to identify catalysts made of abundant elements that reduce the overpotentials required for redox reactions (e.g., CO<sub>2</sub> reduction and the O<sub>2</sub> evolution reaction) at high reaction rates.
- c) Identify materials for thermochemical redox reactions that operate below 1000 °C and are thereby compatible with today's infrastructure in the chemical industry.
- d) Identify and genetically manipulate biological organisms that use non-photosynthetic biocatalysis for CO<sub>2</sub> fixation into chemicals and fuels.
- e) Create new systems architecture and designs for chemical reactors that leverage the research on materials and organisms for CO<sub>2</sub> transformations, and are scalable to the GtCO<sub>2</sub>/yr scale while meeting the cost targets to make cost-competitive chemicals and fuels.
- f) Based on scaled engineered systems analysis in (f), use systems modeling of the global carbon balance (**Appendix 4**) to identify opportunities and challenges for the availability of feedstock, infrastructure and processes (**Appendix 8**) needed for GtCO<sub>2</sub>/yr scale impact.

We also propose that a workshop be held to bring together the science and engineering communities that span the above topics to:

- Identify synergies between seemingly disparate but relevant topics (e.g., carbon-free/neutral exergy, catalysis and reactor design) that are important for CO<sub>2</sub> transformations
- Discuss systems integration and identify tradeoffs in the research goals and targets to produce CO<sub>2</sub> based fuels and chemicals cost competitively.

## References

- Agrafiotis, C., M. Roeb, and C. Sattler. 2015. A review on solar thermal syngas production via redox pair-based water/carbon dioxide splitting thermochemical cycles. *Renewable and Sustainable Energy Reviews* **42**, pp. 254–285
- ARPA-E 2010: <https://arpa-e.energy.gov/?q=arpa-e-programs/electrofuels>
- Barton, E.; Rampulla, D. M.; Bocarsly, A. B. 2008. Selective Solar-Driven Reduction of CO<sub>2</sub> to Methanol Using a Catalyzed p-GaP Based Photoelectrochemical Cell. *J. Am. Chem. Soc.* **130**, pp. 6342-6344.
- DOE Report, 2014. Annual Progress Report of DOE Hydrogen and Fuel Cell Program. [https://www.hydrogen.energy.gov/annual\\_progress14.html](https://www.hydrogen.energy.gov/annual_progress14.html)
- IEA 2013, Technology Roadmap: Energy and GHG Reductions in the Chemical Industry via Catalytic Processes, Report from the International Energy Agency, International Council of Chemical Associations, Dechema
- Jeon, J. H.; Mareswaran, P. M.; Choi, C. H.; Woo, S. I. (2014). Synergism between CdTe semiconductor and pyridine - photo-enhanced electrocatalysis for CO<sub>2</sub> reduction to formic acid. *RSC Adv.* **4**, pp. 3016–3019
- Kantchev, G. and S. Ng, (2015). [Recycling Becomes a Tougher Sell as Oil Prices Drop](#), *Wall Street Journal*, April 5,
- Liebreich, M., 2016, EMEA Future of the Industry, Bloomberg New Energy Finance, Oct. 11. <https://about.bnef.com/presentations/liebreich-state-industry-keynote-emea-summit-2016/>
- Meredig, B., and C. Wolverton, 2009. First principles thermodynamic framework for the evaluation of thermochemical H<sub>2</sub>O- and CO<sub>2</sub>-splitting materials, *Phys. Rev. B* **80**, 2458119.
- Plastics2015: “Plastics – The Facts 2015,” Plastics Europe, Brussels, Belgium. <http://www.plasticseurope.org/plastics-industry/market-and-economics.aspx>
- Plastics2030: [http://www.grida.no/graphicslib/detail/global-plastic-production-and-future-trends\\_b584](http://www.grida.no/graphicslib/detail/global-plastic-production-and-future-trends_b584)
- Scheffe, J. R. and A. Steinfeld. 2014. Oxygen exchange materials for solar thermochemical splitting of H<sub>2</sub>O and CO<sub>2</sub>: a review,” *Materials Today* **17**, pp. 341-348
- Socolow, R., et al. 2011. Direct Air Capture of CO<sub>2</sub> with Chemicals: A Technology Assessment for the APS Committee on Public Affairs, *APS Report*. <http://www.aps.org/policy/reports/assessments/upload/dac2011.pdf>
- Stechel, E.B. and J.E. Miller, 2013. Re-energizing CO<sub>2</sub> to fuels with the sun: Issues of efficiency, scale, and economics” *Journal of CO<sub>2</sub> Utilization*”, *Journal of CO<sub>2</sub> Utilization* **1**, pp. 28 – 36.
- Yuan, J.; Hao, C. 2013. Solar-driven photoelectrochemical reduction of carbon dioxide to methanol at CuInS<sub>2</sub> thin film photocathode. *Sol. Energy Mater. Sol. Cells* **108**, pp. 170–174

## APPENDIX 7

### CARBON DIOXIDE SEQUESTRATION IN GEOLOGIC FORMATIONS

Negative emissions will require sequestering carbon in repositories with long residence times. CO<sub>2</sub> utilization may also require GtCO<sub>2</sub>/yr-scale interim storage of CO<sub>2</sub> to address the mismatch between CO<sub>2</sub> supply and demand for utilization. Presently, underground geological reservoirs are the only option available for millennial time-scale, GtCO<sub>2</sub>/yr-scale sequestration and hence are an essential element of any negative emissions strategy (IPCC, 2005).

Hydrocarbon reservoirs, salt-water filled formations (saline formations), and possibly ultramafic rocks, provide the opportunity for sequestration on the time scales of many tens of thousands to millions of years if the sites are properly selected and managed (IPCC, 2005). Key questions about the GtCO<sub>2</sub>/yr scalability and effectiveness of underground storage include:

- What fraction of the prospective global and regional capacities for storage are going to be available?
- Which are the most secure forms of storage?
- Are there co-benefits such as CO<sub>2</sub>-enhanced oil recovery (CO<sub>2</sub>-EOR) that could enable rapid scaling of the technology?
- For sequestration on the scale of GtCO<sub>2</sub>/yr-scale, what are environmental risks (e.g., leakage, groundwater contamination, induced seismicity) and societal risks (e.g., impacts to land values)?

Here we highlight three opportunities in this regard: reservoir utilization; saline formation storage; and in situ mineralization in ultramafic rocks.

Reservoir Utilization: “Reservoir Utilization” technology uses depleted oil reservoir systems and the underlying salt-water filled aquifers (so-called saline formations) to sequester CO<sub>2</sub> and has the potential store over a GtCO<sub>2</sub>/yr . This opportunity is built on a platform of conventional CO<sub>2</sub> Enhanced Oil Recovery (CO<sub>2</sub>-EOR) and nascent experience with pilot- to medium-sized CO<sub>2</sub> storage projects in saline formations that

have taken place over the past 20 years. For CO<sub>2</sub>-EOR, where the value of incremental oil production has been the economic driving force, the goal has been to minimize storage and maximize utilization of CO<sub>2</sub> to produce oil. If the incentives are changed, such as via a sufficient cost to emit CO<sub>2</sub> into the atmosphere, the goal would reverse to maximizing CO<sub>2</sub> storage. Without a carbon emission cost, this will be very difficult.

*CO<sub>2</sub>-EOR Storage:* In CO<sub>2</sub> Enhanced Oil Recovery, CO<sub>2</sub> is injected into a partially depleted reservoir and increases the flow properties of the residual reservoir oil and thus overall recovery. Through 40 years of extensive experience, the industry has learned how to design CO<sub>2</sub> EOR projects, operate and manage them in a safe and environmentally sound way, and produce incremental oil economically. About half of the CO<sub>2</sub> injected is sequestered within the reservoir and the remaining half is produced with the oil and returned for reinjection, thus recycled. After the CO<sub>2</sub> EOR Project is complete, the CO<sub>2</sub> should remain sequestered underground unless is it intentionally removed for use elsewhere or there is leakage up old wells (Norboten et al., 2009) or weaknesses in the reservoir seal. Understanding the pathways, magnitude, and risks of leakage up old wells is an important issue that needs to be addressed as even small amount of leakage may be significant over the long run.

Today, since CO<sub>2</sub> is a cost to the project, current operations are designed to minimize the sequestration of CO<sub>2</sub>. The value of the produced oil is the economic driving force. Today with low oil prices, little CO<sub>2</sub> EOR is being practiced compared to the potential if large volumes of CO<sub>2</sub> were available. However, 300,000 barrels of oil a day have been produced globally from 140 projects, with a yield of approximately 3 Bbl oil per ton of CO<sub>2</sub> injected into the reservoir. Most of this production has come from the US and particularly from the Permian reservoirs in West Texas. The CO<sub>2</sub> for current operations comes primarily from naturally occurring volcanic formations, in particular from the McElmo Dome and Sheep Mountain formations in the four corners area in the Rocky Mountains. An extensive pipeline system consisting of over 50 individual pipelines and covering 4,500 miles has been developed to move CO<sub>2</sub> from these formations to CO<sub>2</sub>-

EOR projects<sup>23</sup>. The pipeline infrastructure will need to be increased to accommodate more CO<sub>2</sub>-EOR and CO<sub>2</sub> storage.

These projects have been economic based on oil production because of the relatively low-cost CO<sub>2</sub> (\$20-\$30/tCO<sub>2</sub>). As the emphasis on anthropogenic climate change has increased, 13 projects have utilized industrially produced CO<sub>2</sub> for EOR projects (MIT, 2016). Carbon dioxide captured from industrial sources such as natural gas clean-up, ammonia production, gasification, and most recently a coal-fired power plant, have contributed to the CO<sub>2</sub> supply, and now, more than 12 MT/year of the ~50 MT/year used for CO<sub>2</sub>-EOR comes from anthropogenic sources. All of these are developing excellent operating experience for anticipated future carbon pricing policies. The Weyburn-Midale project in Southwest Saskatchewan Canada uses anthropogenic CO<sub>2</sub> from coal gasification for incremental oil production. The project is expected to produce at least 220 million barrels of incremental oil and permanently sequester about 40 MT of CO<sub>2</sub>.

However, in the future with the world targeting the GHG reductions of COP-21, there will be significant incentive to sequester CO<sub>2</sub> if an adequate price for carbon emission is in place. For EOR systems, the economic penalty for emitting CO<sub>2</sub> (and the economic value of sequestering it) would transform the economic incentive from merely maximizing oil production to co-optimizing oil/CO<sub>2</sub> production. At very high CO<sub>2</sub> costs, the objective would be to maximize CO<sub>2</sub> storage in the reservoir system, which includes not only the oil pay zone, but the underlying aquifer as well. The process of co-optimizing was modeled in 2005 at Stanford (Jessen et. al., 2005). They found that changing design parameters such as maximizing the quantity of injection gas CO<sub>2</sub>, tailoring injection profiles to reservoir character, and optimizing water injection could increase CO<sub>2</sub> storage significantly in the reservoir itself. Further enhancements could be obtained by CO<sub>2</sub> injection into horizontal wells in the aquifers underlying the oil fields.

In IEA's 2015 study "Storing CO<sub>2</sub> through Enhanced Oil Recovery," reservoir/aquifer storage was modeled further, and results indicated that storage could be increased by a

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<sup>23</sup> U.S DOE, 2015. A Review of CO<sub>2</sub> Pipeline Infrastructure in the United States. DOE/NETL-2014/1681.

factor of 3 over a base case compared to conventional EOR provided there is a GHG emissions charge (IEA, 2015). These high storage volumes could potentially be accomplished by not re-reinjecting produced water into the reservoir and by injecting the CO<sub>2</sub> once through into both the reservoir (for oil recovery) and into the saline aquifer below the reservoir - *thus a Reservoir Utilization approach*. The USGS and DOE have estimated there are 60 -120 GtCO<sub>2</sub> storage capacity in depleted reservoir systems in the US and thus significant storage capacity exists (USGS, 2013; USDOE, 2012). Additional storage capacity might be achieved through R&D strategies not considered in current storage capacity estimates for depleted oil reservoirs. And the DOE-led Regional Carbon Sequestration Partnership (RCSP) has mapped and assessed the potential EOR storage sites in the US. Untapped and poorly understood opportunities exist in expanding the range of reservoirs suitable for CO<sub>2</sub> to include immiscible CO<sub>2</sub> floods, CO<sub>2</sub> exsolution, and indeed, rejuvenate oilfields that are no longer productive (Alizadeh et al., 2011; Zuo and Benson, 2013; Hatchell and Benson, 2016). R&D to develop these new concepts is needed.

In the short term, to achieve GT/year rates of CO<sub>2</sub> in reservoir systems, scale-up of the number of CO<sub>2</sub>-EOR/storage projects by the oil and gas industry will be the limiting factor in oil reservoirs. Many well-understood opportunities exist around the world (Godec et al., 2011). Based on screening a data base of the world's largest basins for CO<sub>2</sub>-EOR potential, Godec et al. (2011) estimated that 470 billion barrels could be recovered from fields favorable for miscible CO<sub>2</sub>-EOR, and could facilitate the storage of 140 GtCO<sub>2</sub>. For reservoir systems, infrastructure for drilling wells, and operating experience and permitting procedures already exist which can greatly accelerate scale up. There are significant economies of scale and challenges in developing right-of-ways for pipeline transport of CO<sub>2</sub> (McCoy and Rubin, 2009). Developing a shared network linking CO<sub>2</sub> sources to CO<sub>2</sub> storage sites could accelerate scale-up, but the private sector is unlikely to do this in the absence of a long-term and certain policy about a price on carbon emissions.

*Saline Formations:* The largest prospective capacity for CO<sub>2</sub> storage lies in saline aquifers. An estimated 2,000 to 21,000 GtCO<sub>2</sub> of prospective storage capacity exists in saline formations in North America (NETL, 2015), but the precise amount of storage capacity and the best locations for storing CO<sub>2</sub> remain uncertain because most of these storage formations have not been thoroughly characterized. Suitable storage reservoirs have many requirements. They must be deep enough to store CO<sub>2</sub> in the supercritical phase (> 1 km deep), permeable enough (>10<sup>-14</sup> m<sup>2</sup>) enough to inject CO<sub>2</sub> at rates on the order of 1 MT/year, porous enough (>10% porosity) to accommodate a reasonable volume of CO<sub>2</sub>, have salinity exceeding 10,000 ppm (that is, not contain potable water) and preferably multiple sealing formations (e.g. shale, anhydrite, dolomite) without faults and with a low enough permeability (<10<sup>-17</sup> m<sup>2</sup>) and high enough capillary entry pressure to prevent leakage (Miocic et al, 2016). Developing reliable, cost effective, and rapid methods for characterizing storage sites is a big priority for accelerating the scale-up of saline formation storage. Saline aquifers that meet these criteria are unlikely to experience the long-term leakage rates of EOR projects because the lack the large number of wells that are typically drilled into oil reservoirs.

In addition to the seal, storage security is further enhanced by secondary trapping mechanisms such as dissolution into the saline fluids in the reservoir, residual gas trapping, and mineralization. Over the past decade R&D support from governments and industry has dramatically increased fundamental understanding of these processes (as documented in Krevor et al., 2015, Emami-Meybodi et al., 2015, and Birkholzer et al., 2015). DOE-supported EFRCs are using the most advanced nano- to micro-scale techniques for understanding these processes. Supercomputers are being used to scale up this knowledge to the reservoir scale. Still, questions remain about the coupled interplay between these processes in inherently heterogeneous rocks over the timescale of millennia. So, R&D is needed to increase confidence in these secondary trapping processes, particularly to accelerate the pace of scale-up by expanding the range of suitable sites to include those which fundamentally rely on them. This is important government enabling R&D.

Some risks of geological storage also remain poorly understood. In particular, the influence of regional pressure buildup caused by CO<sub>2</sub> injection is uncertain. If CCS is scaled up rapidly, it is likely that multiple storage projects will take place in the same saline formation. The cumulative effect of multiple storage projects is likely to cause widespread pressure buildup in the storage formation (Birkholzer et al., 2015). Under these circumstances, induced seismicity such as has occurred in Oklahoma in association with large scale water injection may occur. Similarly, shallow groundwater contamination by brine displacement up abandoned wells or through large faults is another concern. The potential for these to occur and mitigation actions to avoid them require R&D.

Finally, monitoring is another key component of assuring safe and effective storage. The large number of pilot-scale projects supported by governments and commercial projects supported by industry have resulted in an explosion of monitoring technology. Now, a wide variety of monitoring tools are available for tracking CO<sub>2</sub> plume migration in the storage reservoir, detecting leakage in overlying aquifers, measuring changes in groundwater quality, geomechanical deformation, induced seismicity, and surface leakage. Drawing from the sophisticated suite of seismic, electrical resistivity, InSar, tilt, pressure, chemical, tracer, and gas flux monitoring, “fit-for-purpose” monitoring programs are being developed. In spite of this outstanding progress, new, better, and cheaper techniques are emerging and in this era of big data, new low-cost sensors, satellite observing systems and drones, there is a huge opportunity to support the rapid scale-up of CCS up by new monitoring technologies and approaches and to help understand the risk and extent of leakage from old wells.

This SEAB Task Force believes that CO<sub>2</sub> storage in oil and gas reservoirs and saline formations has potential for GT/year CO<sub>2</sub> storage. Much progress has been made over the past 20 years, but a 50-fold scale-up of the global CCS endeavor is required to get to the GT/year scale (see Figure A7.1). But, it could be scaled up faster than most other deep decarbonization technologies because it is built on a platform of existing

operations and infrastructure. From a RD&D standpoint, the program to accelerate scale-up would need to proceed along parallel paths.

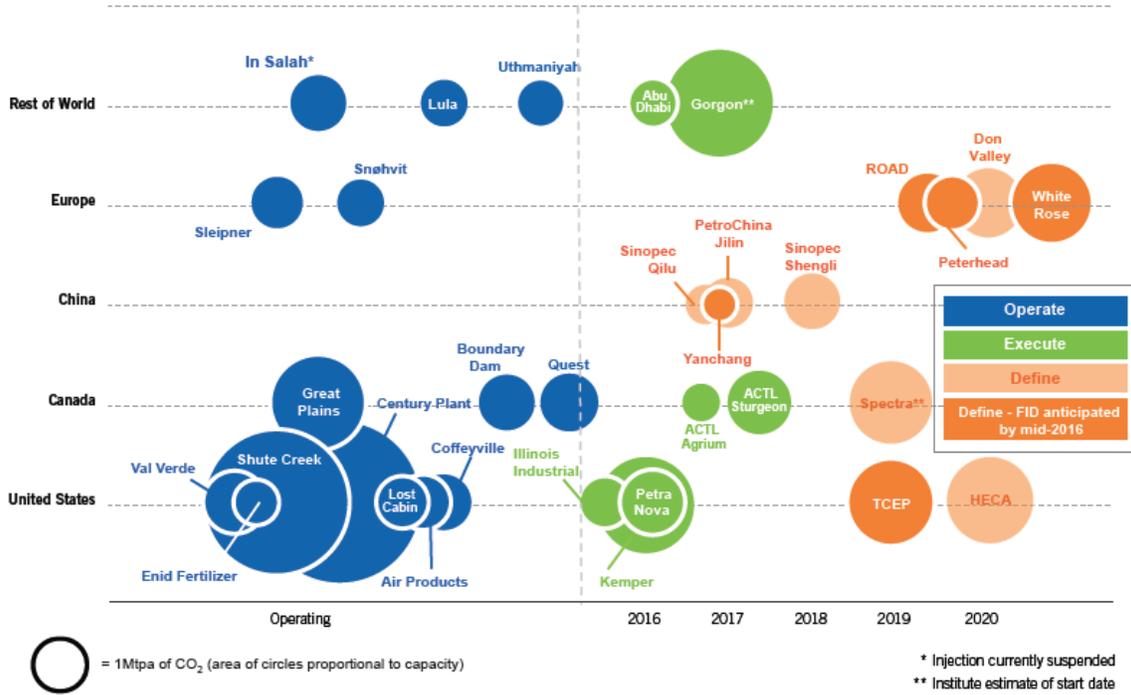
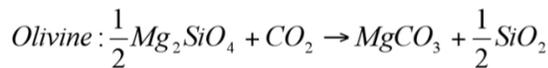
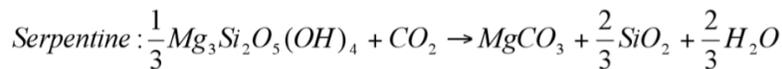


Figure A7.1. Existing and planned CCS projects (GCCSI, 2015).

In-Situ Mineralization: Carbon dioxide reacts with ultramafic rocks such as dunite (olivine), peridotite, harzburgite, wehrlite, lherzolite, picrite, and their altered form, serpentinite to form stable carbonate minerals (Lackner et al., 1995). Ultramafic rocks are characterized by low silica content of less than 45% and an abundance of magnesium. Mapping of these types of rocks show that while they are not widespread, the quantities are large (Krevor et al., 2009). The reaction of CO<sub>2</sub> with minerals in these rocks are well known and an important component of the natural geological cycle process of “weathering.” Examples of carbonation reactions for olivine and serpentine are:



Basaltic rocks also contain an abundance of calcium and magnesium-rich minerals and undergo similar reactions when exposed to CO<sub>2</sub> (McGrail et al., 2006).

There is considerable interest in storing CO<sub>2</sub> by reacting it with ultramafic and basaltic rocks because it provides carbon storage in stable carbonate minerals. In addition, some regions of the world lack geological formations for conventional CO<sub>2</sub> storage (e.g., much of India) and basalts/ultramafic rocks may provide an alternative option for storage.

Early research on mineral carbonization focused largely on ex situ mineralization, but the energy requirements, large volumes of rocks required for these reactions, and slow kinetics made this impractical (IPCC, 2005).

Subsequently, the emphasis for mineral carbonation of CO<sub>2</sub> switched to focus on in situ mineralization. If CO<sub>2</sub>, or CO<sub>2</sub> dissolved in water, could be injected into these rocks, and remain underground long enough to undergo these reactions, this may provide a promising option for C sequestration. A recent experiment conducted in the basaltic rocks on Iceland produced encouraging results demonstrating that these reactions occurred more quickly than expected (Matter et al., 2016). If practical engineering schemes could be implemented to harness and sustain these in situ mineralization reactions, the potential for carbon sequestration is large.

To date, the R&D efforts devoted to understanding the fundamental science and practical approaches for in situ mineralization have been limited. An expanded R&D effort is needed to determine whether or not this offers Gt/year potential for carbon sequestration.

The Task Force makes recommendations in four categories: cross-cutting; reservoir utilization; saline formations; and in situ mineralization.

Cross-Cutting Issues:

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- a) Develop and execute a roadmap for accelerating CO<sub>2</sub> storage and reservoir utilization from high-purity anthropogenic CO<sub>2</sub> emission sources where there are some immediate opportunities<sup>24</sup>.
- b) Create and support a Data Commons<sup>25</sup> as a shared resource for the research community to document CO<sub>2</sub> injection, storage, oil recovery, brine recovery and any other relevant information that would be helpful to collectively understand and investigate effective co-optimization and storage techniques.
- c) Develop and implement a monitoring, measurement, and verification system capable of accurately predicting multiple century CO<sub>2</sub> leakage rates and environmental impacts of carbon capture, utilization, and storage (CCUS) projects. This is essential to increase the confidence needed by all stakeholders (e.g., project operators, financiers, regulators, insurers, and communities) to initiate and sustain the rapid scale-up of GtCO<sub>2</sub>/yr scale reservoir utilization and saline formation storage.

### Reservoir Utilization:

- d) Intensify and expand the RD&D program to:
  - i. Develop fundamental understanding of mechanisms of pore scale CO<sub>2</sub> displacements, including immiscible displacements and other novel CO<sub>2</sub>-EOR schemes, and flow in a broad class of reservoirs beyond CO<sub>2</sub>-EOR.
  - ii. Co-optimize of CO<sub>2</sub>-EOR and CO<sub>2</sub> storage in hydrocarbon reservoirs and underlying saline formations.
  - iii. Develop an approach to estimate reservoir storage costs and operating parameters for different types of reservoir systems.
  - iv. Estimate infrastructure needs such as pipelines between storage sites and CO<sub>2</sub> sources, and create a roadmap in terms of costs, rates and timings for scale up.
- e) In the absence of a carbon emission charge, conduct jointly funded pilot-scale and demonstration projects with the hydrocarbon industry and research community (academic and national laboratory) to test co-optimization techniques and expand

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<sup>24</sup> Studies have identified that there are high-purity sources at the scale of 30 MT-CO<sub>2</sub> that can be captured at \$30/tCO<sub>2</sub>. [http://energy.gov/sites/prod/files/2016/09/f33/DOE%20-%20Carbon%20Capture%20Utilization%20and%20Storage\\_2016-09-07.pdf](http://energy.gov/sites/prod/files/2016/09/f33/DOE%20-%20Carbon%20Capture%20Utilization%20and%20Storage_2016-09-07.pdf)

<sup>25</sup> Data sharing could be obligatory for all government contracts and joint studies involving government funding. Special provisions need to be made to protect propriety data from oil and gas-field operators. Responsibilities of data users should be clearly spelled out in access agreements. Compliance on the part of data generators and users should be monitored for compliance with the access policies

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the range of hydrocarbon reservoirs where CO<sub>2</sub> storage is attractive. Put all of the quality assured data from this project into the Data Commons consistent with the requirements of the contract.

### Saline Formations:

- f) Continue and strengthen the R&D program to understand and harness secondary trapping mechanisms, site characterization, and geomechanical effects to assure safe and effective GtCO<sub>2</sub>/yr scale storage on century to millennium time scales.
- g) Address important questions of leakage (or integrity of seals), accuracy of models for long-term performance, risk of seismicity, efficacy of monitoring to detect leakage and groundwater contamination.

### In-Situ Mineralization

- h) An expanded R&D effort is needed to determine whether or not our fundamental understanding of CO<sub>2</sub> mineralization offers GtCO<sub>2</sub>/year potential for carbon sequestration. Convening a team of scientists and engineers to identify the full range of opportunities and challenges is a logical first start.

## References

- Benson, S. M., K. Bennaceur, P. Cook, J. Davison, H. de Coninck, K. Farhat, A. Ramirez, D. Simbeck, T. Surles, P. Verma, and I. Wright. 2012. Carbon capture and storage. Chapter 13 in *Global Energy Assessment-Toward a Sustainable Future*. Cambridge, UK: Cambridge University Press.
- Birkholzer, J. T., Oldenburg, C. M., & Zhou, Q. 2015. CO<sub>2</sub> migration and pressure evolution in deep saline aquifers. *International Journal of Greenhouse Gas Control*, **40**, pp. 203-220.
- Emami-Meybodi, H., Hassanzadeh, H., Green, C. P., & Ennis-King, J. 2015. Convective dissolution of CO<sub>2</sub> in saline aquifers: Progress in modeling and experiments. *International Journal of Greenhouse Gas Control* **40**, pp. 238-266.
- GCCSI, 2015. The Global Status of CCS, 2015.
- Godec, M., Kuuskraa, V., Van Leeuwen, T., Melzer, L. S., & Wildgust, N. (2011). CO<sub>2</sub> storage in depleted oil fields: the worldwide potential for carbon dioxide enhanced oil recovery. *Energy Procedia* **4**, pp. 2162-2169.
- Hepple, R. P., and S. M. Benson. 2005. Geologic storage of carbon dioxide as a climate change mitigation strategy: Performance requirements and the implications of surface seepage. *Environmental Geology* **47**(4), pp. 576-585. DOI: 10.1007/s00254-004-1181-2.
- IEA. 2013. Technology Roadmap: Carbon Capture and Storage.

- Krevor, S. C., Graves, C. R., Van Gosen, B. S., & McCafferty, A. 2009. *Mapping the mineral resource base for mineral carbon-dioxide sequestration in the conterminous United States*. US Geological Survey.
- Matter, J. M., Stute, M., Snæbjörnsdóttir, S. Ó., Oelkers, E. H., Gislason, S. R., Aradóttir, E. S., ... & Axelsson, G. 2016. Rapid carbon mineralization for permanent disposal of anthropogenic carbon dioxide emissions. *Science* **352**(6291), pp.1312-1314.
- McGrail, B. P., Schaef, H. T., Ho, A. M., Chien, Y. J., Dooley, J. J., & Davidson, C. L. 2006. Potential for carbon dioxide sequestration in flood basalts. *Journal of Geophysical Research: Solid Earth* **111**, B12201.
- Metz, B., Davidson, O., De Coninck, H., Loos, M., & Meyer, L. 2005. Carbon dioxide capture and storage. IPCC Report Working Group III <http://digital.library.unt.edu/ark:/67531/metadc12051/>.
- MIT 2016. <https://sequestration.mit.edu/>
- NETL, 2015. 5<sup>th</sup> Carbon Storage Atlas. <https://www.netl.doe.gov/research/coal/carbon-storage/atlasv>
- Nordbotten, J. M., Kavetski, D., Celia, M. A., & Bachu, S. 2009. Model for CO<sub>2</sub> leakage including multiple geological layers and multiple leaky wells. *Environmental science & technology* **43**(3), pp. 743-749.
- USDOE 2012. <http://energy.gov/fe/articles/does-carbon-utilization-and-storage-atlas-estimates-least-2400>
- USGS 2013. [https://www2.usgs.gov/blogs/features/usgs\\_top\\_story/the-gigaton-question-how-much-geologic-carbon-storage-potential-does-the-united-states-have/](https://www2.usgs.gov/blogs/features/usgs_top_story/the-gigaton-question-how-much-geologic-carbon-storage-potential-does-the-united-states-have/)

## APPENDIX 8

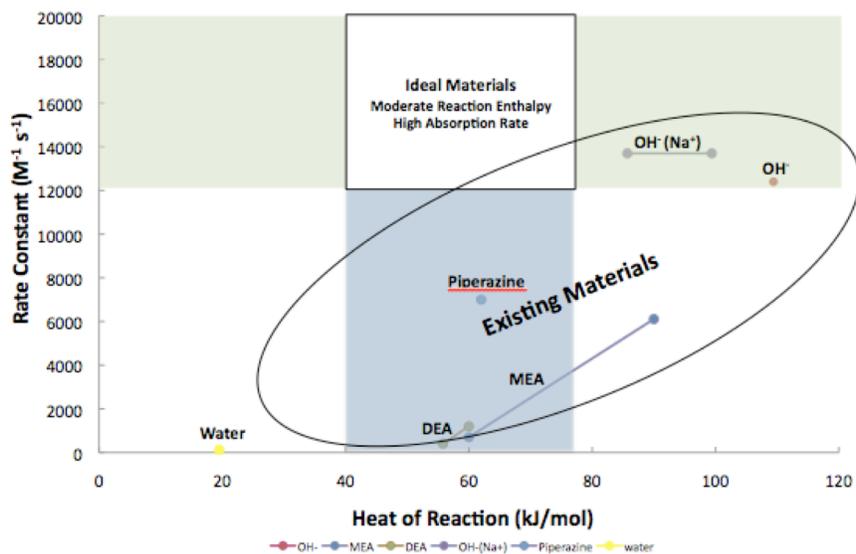
CO<sub>2</sub> CAPTURE AND OTHER SEPARATION TECHNOLOGIES

Any separation of CO<sub>2</sub> from a mixture of gases requires energy to overcome the entropy of mixing. The predominant approach today is via binding reactions to sorbent molecules ( $A + CO_2 = A:CO_2$ ), followed by removal of the bound CO<sub>2</sub> from the mixture, unbinding of CO<sub>2</sub> from the sorbent molecule (A), and finally reuse of the sorbent molecule (Wilcox, 2012; Smit et al, 2014). The thermodynamics of the binding and unbinding reactions are governed by Gibb's free energy  $\Delta G = \Delta H - T\Delta S$ , where  $\Delta H$  is the enthalpy of the reaction,  $\Delta S$  is the entropy change, and  $T$  is the temperature. Since the binding reaction results in  $\Delta S < 0$ , the reaction must necessarily be exothermic ( $\Delta H < T\Delta S < 0$ ) for the reaction to occur ( $\Delta G < 0$ ). For the dissociation reaction  $\Delta S > 0$  and  $\Delta H > 0$  and hence one needs to raise the temperature  $T$  such that  $T\Delta S > \Delta H$  such that again  $\Delta G < 0$ . The equilibrium temperature for dissociation is therefore,  $T_d = |\Delta H|/|\Delta S|$ .

While the thermodynamics of individual reactions is well understood, what is often overlooked is the fact that CO<sub>2</sub> has to compete with other molecules (D) in the mixture (e.g., H<sub>2</sub>O) to bind to the sorbent (A). The selectivity of binding is related to the ratio  $[CO_2]K_{CO_2}/[D]K_D$  where  $[CO_2]$  and  $[D]$  are the concentrations of CO<sub>2</sub> and the competing molecule D, respectively, and  $K$  is the equilibrium constant  $K \propto \exp(-\Delta G/RT)$  where  $R$  is the universal gas constant. As is evident, if the concentration  $[D] \gg [CO_2]$  and we want selectivity to CO<sub>2</sub> binding, then we must have  $[CO_2]K_{CO_2} \gg [D]K_D$ . Therefore, it is necessary to have  $|\Delta G_{CO_2}| > |\Delta G_D|$  for the sorbent to selectively bind to CO<sub>2</sub>. This naturally suggests that for preferential binding to CO<sub>2</sub>, the reaction between A and CO<sub>2</sub> should be highly exothermic ( $|\Delta H_{CO_2}| \gg |\Delta H_D|$ ). However, this has the undesirable impact that  $T_d$  will be high, requiring high energy input for the dissociation reaction. This increases the energy or the *operating cost* of CO<sub>2</sub> capture and separation. One might then conclude that relatively weak CO<sub>2</sub> binding – still necessarily larger than D's binding - is preferable. However, the binding cannot be too weak, not only because of the selectivity issue already mentioned, but also because the association-dissociation equilibrium would then require increased partial pressures of CO<sub>2</sub> to achieve sufficient

binding to effectively capture it. Increasing pressure on the front end raises the energy requirement for operation, with the mechanical energy of compression as a new consideration in the tradeoff of energy inputs for capture and release. Thus there is a sweet spot, as indicated in the figure below, of preferred binding exothermicity.

The rates of reaction are also important for cost estimation, and are given by  $r = k_f[A][CO_2] - k_r[A:CO_2]$  where  $k_f$  ( $M^{-1}s^{-1}$ ) and  $k_r$  ( $s^{-1}$ ) are the rate constants for the forward and reverse reactions, and  $K = k_f/k_r$ . If  $k_f \gg k_r$ , the forward reaction is strongly favored and hence a single pass through of  $CO_2$  over the sorbent will capture much more  $CO_2$  than if  $k_f \sim k_r$ . Therefore, to capture the same amount of  $CO_2$ , the reactor size and the cost is lower if  $k_f \gg k_r$ . The key point to note is that the reactor size is inversely proportional to the reaction rate constant, which has direct impact on the *capital cost* of a  $CO_2$  capture plant.



**Figure A8.1:** Rate constant (liter/mol-sec) vs. absolute value of the reaction enthalpy (kJ/mol) for chemical sorbents. Source: APS Report, Figure 3B.1, p. 69.

Thus, an ideal sorbent for  $CO_2$  is one that has high  $k_f$  and moderate  $\Delta H$ . However, Fig. A8.1 suggests that for current sorbents such as monoethanol amine (MEA), sodium hydroxide (NaOH), and others, the rate constants and enthalpy are correlated.

Currently, there are no sorbents which possess  $k_f > 12000 \text{ M}^{-1}\text{s}^{-1}$  and  $|\Delta H| < 70 \text{ kJ/mol}$ . This ought to be part of a research effort to identify sorbents in this thermodynamic and kinetic range. Perhaps one option is to introduce weak (low  $\Delta H$ ) multivalent or cooperative binding for high selectivity, an approach often found in biology. But because  $\text{CO}_2$  is a small molecule this is difficult, unless it is possible to exploit the quadrupole moment of  $\text{CO}_2$  molecules. Selectivity of  $\text{CO}_2$  binding may also be able to take advantage of the  $\pi$ -electron system of  $\text{CO}_2$ , to consider binding, e.g., to aromatic amines such as bipyridine (Benson et al., 2013; Keith et al., 2013).

It is worth noting  $\text{CO}_2$  concentrations in the atmosphere are much lower than those of the point sources (e.g., post-combustion capture from coal-fired or natural gas power plants). Hence, the condition  $[\text{CO}_2]K_{\text{CO}_2} \gg [\text{D}]K_{\text{D}}$  is more difficult to be met for direct air capture than that used for point sources. On the other hand, if R&D yields sorbents that satisfy the condition for direct air capture,  $\text{CO}_2$  capture from point sources would be solved as well.

While absorption in liquids offers a volumetric advantage that adsorption on solid surfaces lacks, the conventional choices of alcohol amines or alkali hydroxides have the significant disadvantage that they are dissolved in water, a substance with high heat capacity. As a result, the Achilles heel of these solutions is the enormous amount of energy required simply to heat up the water – that comprises the largest component of these solutions - to release the  $\text{CO}_2$ . Thus, R&D is needed to identify new liquid solutions with lower heat capacity than water that can selectively bind  $\text{CO}_2$  in the sweet spot of rates and enthalpies mentioned above. Such liquids need to be non-corrosive, non-viscous, and inexpensive. Ionic liquids (ILs) have been pursued as alternatives, largely because of their potential reduced energy demands during solvent regeneration (Boot-Handford et al., 2014). Other positive features of ILs include tunability of both anions and cations to optimize temperature/pressure swing absorption/desorption, increased solubility and diffusivity of  $\text{CO}_2$  due to a potentially more open network nature, high thermal stability and low vapor pressure that enables operation over a wide temperature range. Their main disadvantages are higher viscosity – resulting in lower

heat and mass transfer - and simply the expense of designer materials at the scales required. Their high viscosity can be overcome by using supported ion-liquid membranes (SILMs), which increase the contact area while maintaining high stability; moreover, SILMs are easily regenerated and pose less environmental hazards than the ILs themselves. For ILs and other novel capture agents, materials discovery research that optimizes for physical properties subject to actual costs at scale are needed.

SILMs are effectively one type of adsorption-based solids, which can retain a high heat of adsorption to enhance selectivity and capture rate, while employing a medium with a much lower heat capacity than aqueous solutions. Adsorbents ideally should be able to work at low pressure, be selective, exhibit fast kinetics, and be stable mechanically, thermally, and with respect to humidity. Synthesis and characterizations of nanoporous carbons, amine-modified mesoporous silicas, zeolites, metal-organic frameworks (MOFs), polymeric membranes, and other media that enable tuning of CO<sub>2</sub> binding enthalpies and rates ( $\Delta H$  and  $k_f$ ) are active areas of basic research that should be continued, subject to the economic constraint mentioned above. MOFs offer, like ILs, a veritable playground of tunability, because of the diverse building blocks of metals and organic linkers that one can use to create them. They feature very high surface area that enable increased adsorption. As with zeolites, tunability of gas separation selectivity is outstanding due to fine control of molecular binding and transport. Activated carbons are more stable hydrothermally than zeolites and have low heats of adsorption, but exhibit less capacity and selectivity. In some instances, these tradeoffs may still favor their use. Organic polymers possess versatility characteristics similar to MOFs and can be isolated as solids. CO<sub>2</sub> can be held in internal cavities via host-guest interactions optimized for chemical selectivity, absorption capacity, and permeability.

Finally, we recommend continued research into the discovery of catalysts that accelerate binding of CO<sub>2</sub>, including conversion of CO<sub>2</sub> to carbonate or bicarbonate. Mimics of carbonyl anhydrase are but one example. These could be used with both liquid and solid absorbents.

Membrane separations have the potential to displace high-temperature, energy-intensive processes such as distillation and evaporation. Key to separation of gas mixtures is a fine balance between the membrane's selectivity and permeability for CO<sub>2</sub>, as already alluded to in the discussion of solid absorbents and SILMs above. Separation of liquid mixtures containing molecules of similar polarity, as arises biofuel production and CO<sub>2</sub> reduction to alcohols, poses a particular challenge. While a variety of separation technologies exist for ethanol-water and butanol-water mixtures, no successful process yet exists for methanol-water mixtures that arise from photocatalytic reduction of CO<sub>2</sub> by certain compound semiconductors in the presence of aromatic amine co-catalysts (see **Appendix 6**). An example of a promising separation technology is pervaporation, in which both permeability and vapor pressure differences are exploited (Van der Bruggen and Luis, 2014). More research into materials and process discovery for miscible liquid mixture separations is clearly needed.

Based on this background the SEAB CO<sub>2</sub> Task Force makes the following recommendations. Create a research program to:

- a) Identify new, low-cost CO<sub>2</sub> sorbents made of abundant elements that have a binding enthalpy  $|\Delta H| < 70$  kJ/mol, binding rate constant  $k_f > 12000$  M<sup>-1</sup>s<sup>-1</sup>, and  $k_f \gg k_r$ , where  $k_r$  is the rate constant for the unbinding or dissociative reaction. A lower enthalpy correlates to lower energy costs whereas higher binding rate constant correlates to smaller plant size and thereby lower capital costs. Current sorbents have either: (a) high rate constants and high binding enthalpy, and thereby high energy costs; or (b) low rate constants and low enthalpy, and thereby high capital costs.
- b) Identify new, low-cost, noncorrosive, non-viscous liquid solutions with lower heat capacity than water that selectively bind CO<sub>2</sub> with the characteristics in (a).
- c) Discover new materials and processes to separate miscible liquid mixtures optimized for very low capital and operating costs.
- d) Design, build and demonstrate scalable reactor designs that offer the possibility to substantially reduce carbon capture and separation costs.

- Benson, E. E., M. D. Sampson, K. A. Grice, J. M. Smieja, J. D. Froehlich, D. Friebe, J. A. Keith, E. A. Carter, A. Nilsson, and C. P. Kubiak, 2013. The Electronic States of Rhenium Bipyridyl Electrocatalysts for CO<sub>2</sub> Reduction as Revealed by X-Ray Absorption Spectroscopy and Computational Quantum Chemistry," *Angew. Chem. Int. Ed.* **52**, 4841-4844.
- Boot-Handford, M. E., J. C. Abanades, E. J. Anthony, M. J. Blunt, S. Brandani, N. MacDowell, J. R. Fernandez, M.-C. Ferrari, R. Gross, J. P. Hallett, R. S. Haszeldine, P. Heptonstall, A. Lyngfelt, Z. Makuch, E. Mangano, R. T. J. Porter, M. Pourkashanian, G. T. Rochelle, N. Shah, J. G. Yao, and P. S. Fennell. 2014. Carbon capture and storage update, *Energy Environ. Sci.*, **7**, pp. 130-189.
- Keith, J. A., K. A. Grice, C. P. Kubiak, and E. A. Carter. 2013. Elucidation of the Selectivity of Proton-Dependent Electrocatalytic CO<sub>2</sub> Reduction by *fac*-Re(bpy)(CO)<sub>3</sub>Cl. *J. Am. Chem. Soc.* **135**, pp. 15823-15829.
- Smit, B., J. R. Reimer, C. M. Oldenburg and I. C. Bourg. 2014. *Introduction to Carbon Capture and Sequestration*, Imperial College Press, London.
- Van der Bruggen, B. and P. Luis. 2014. Pervaporation as a tool in chemical engineering: a new era?, *Curr. Op. Chem. Eng.* **4**, pp. 47-53.
- Wilcox, J. 2012. *Carbon Capture*, Springer, New York.

**APPENDIX 9**DIRECT AIR CAPTURE OF CO<sub>2</sub> WITH CHEMICALS

Many chemicals can selectively remove CO<sub>2</sub> from a gas mixture (see **Appendix 8**), including from air. Direct Air Capture (DAC) describes these chemical approaches (Keith, 2009). To take a simple example, when air is blown over sodium hydroxide (NaOH), the CO<sub>2</sub> in the air selectively reacts to produce sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>). Na<sub>2</sub>CO<sub>3</sub> is subsequently processed to produce CO<sub>2</sub> at a higher concentration – as well as NaOH, which is recycled. The net effect is to concentrate CO<sub>2</sub> but not to change it chemically. What happens subsequently to the concentrated CO<sub>2</sub> is not part of DAC: it may be used as CO<sub>2</sub> in concentrated form, or transformed by chemical reactions into other molecules, or sequestered. DAC in combination with sequestration is, in essence, a way of scrubbing the atmosphere of some of its CO<sub>2</sub> and lowering its concentration.

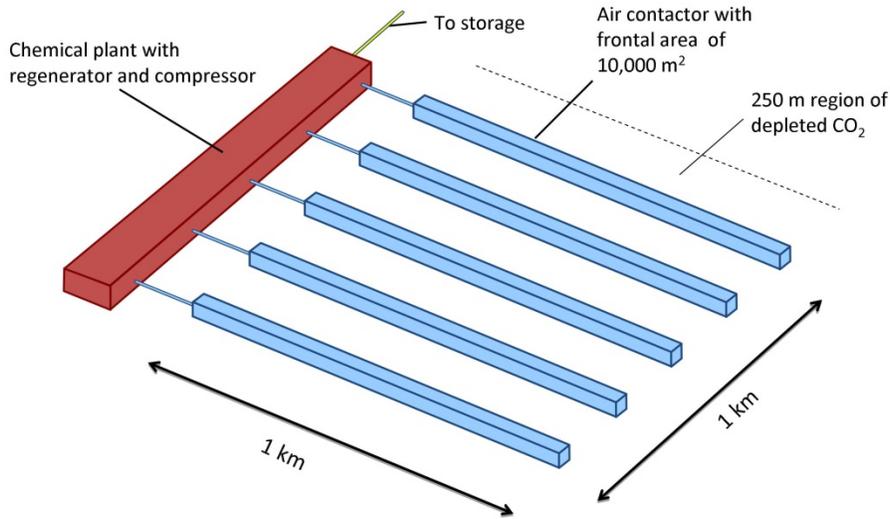
Biological approaches to CO<sub>2</sub> capture are different from DAC, in that the selective removal of CO<sub>2</sub> from the air is accompanied by chemical reactions that change the CO<sub>2</sub> into other molecules (sugars, for example). The advantages of DAC accrue as a result of its *not* involving biological processes and, thereby, not being in conflict with other uses of land – to grow food and provide habitat, for example. DAC can be located at sites that are unsuitable for biology. DAC does not have the seasonality of biological processes that are characteristic of many locations, either.

DAC presents many challenges (Socolow et al., 2011). We distinguish here inevitable problems, researchable problems distinct for DAC, and researchable problems widely found across CO<sub>2</sub> removal strategies.

Inevitable Problems: The principal inevitable problem with DAC is that a very large amount of air must be intercepted. One GtCO<sub>2</sub> is contained in about 1700 Gt air, since CO<sub>2</sub> is present at a molar concentration of 400 ppm, which is 600 ppm by weight; the air occupies  $1.4 \times 10^{15}$  m<sup>3</sup>. If half of the CO<sub>2</sub> passing over the absorbers is removed and half passes through without reacting, then  $2.8 \times 10^{15}$  m<sup>3</sup> of air would need to pass over the

absorbers. If this were to happen in one year, and if the flow rate through the system were 2 m/s, the area crosswise to the air flow through which the air would need to flow would need to be  $5 \cdot 10^7 \text{ m}^2$ . This is a very large amount of engineered space – a structure 10 meters high and 5,000 kilometers long. However, as Lackner has pointed out (Lackner et al., 2012), this area is considerably less than the area that must be intercepted by wind turbines to cancel out 1 GtCO<sub>2</sub>/yr produced by coal plants, when wind power substitutes for coal power.

Figure A9.1 shows an array of five buildings on a 1 km x 1 km parcel of land that removes 1 MtCO<sub>2</sub>/yr from the atmosphere, with the same assumptions that air flows through the structures at 2 m/s and that half of the CO<sub>2</sub> is captured. To remove 1 GtCO<sub>2</sub>/yr would require one thousand of these projects. To cancel the emissions of a 1 GW coal plant would require about six of them.



**Figure A9.1:** Schematic representations of a facility for capturing 1 MtCO<sub>2</sub>/yr. The facility could collect 1 MtCO<sub>2</sub>/yr if air passed through at 2 m/s and 50% of the CO<sub>2</sub> were collected. It has five structures, each 10 meters high and 1 km long, and the structures are spaced 250 meters apart. Approximately six of these systems would be required to compensate for the emissions of a 1 GW coal plant. Buildings not to scale. Source: APS Report, Figure 1.2B, p. 8.

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Researchable Problems Distinct for DAC: The two most important steps in DAC are achieving a large contact area for the capture reaction and regenerating the sorbent. Both are research areas. To achieve large contact area, some concepts envision the passage of air through large volumes of mesh, others envision passage through a porous ceramic. The air velocity is an important independent variable.

The endpoint of a DAC system can be CO<sub>2</sub> at various levels of concentration and purity. In principle, concentration can be in stages (say from 400 ppm to 1 percent in one device and from 1 percent to 99 percent in a second device).

As for sorbent regeneration, one can ask first if regeneration is necessary. In principle, the sorbent can be discarded, bonded to CO<sub>2</sub>, rather than regenerated. But 1 GtCO<sub>2</sub>/yr capture without regeneration will involve on the order of 1 Gt/yr of sorbent throughput, which would entail huge materials flow in and out and have major implications for sorbent fabrication and end-product disposal. So, almost surely, the sorbent must be recycled. Further, the volume of sorbent required is enormous. For example, the quantity of hydroxide required vastly exceeds US production.

Further research challenges specific to DAC address the impact of environmental conditions on performance. Performance includes durability of materials, as well as reaction rates and material flows. Many harsh environments can be imagined, from a dry and cold arctic site to a moist and hot site in the tropics.

Another issue is CO<sub>2</sub> replenishment after depletion, downstream of a collecting structure. Figure A9.1 shows two identical systems, one of them 250 meters downstream from the other. No modeling lies behind this choice of spacing.

Problems in common with all other CO<sub>2</sub> removal strategies: “Net carbon” can be a severe challenge for all systems that extract CO<sub>2</sub> from the atmosphere. Numerous steps require chemical, mechanical, electrical, or thermal energy. Biological systems may require fertilizing, plowing, harvesting, drying, and transport. DAC may require

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fanpower, heating, and drying. Both require the construction of buildings and equipment. How much CO<sub>2</sub> is released to the air during the provision of these functions is likely to be critically dependent on the carbon intensity of the energy system providing these services. CO<sub>2</sub> removal may emit more CO<sub>2</sub> than is captured, if conducted in the near term with a carbon-intensive energy system, but be net negative even conducted in the same way but at a later time if the energy system meanwhile becomes substantially less carbon-intensive.

The earth's carbon cycle becomes involved when CO<sub>2</sub> is removed from the atmosphere (**Appendix 4**). Should one expect outgassing of the oceans, given that CO<sub>2</sub> emissions to the atmosphere produces CO<sub>2</sub> flow from the atmosphere into the oceans? (If so, the ocean pH would increase.) What about forests and other locations of terrestrial carbon stock on land, which are currently increasing in mass – probably at least in part because extra CO<sub>2</sub> in the atmosphere promotes plant growth (carbon fertilization)? These are researchable questions of broad importance for CO<sub>2</sub> capture from air, no matter how accomplished.

Additional remarks: The CO<sub>2</sub> concentration in the flue gas at a coal power plant is about 12 percent by volume, 300 times greater than in air. For natural gas power plants, the ratio is about 100. Although solutions for flue-gas capture and air capture may sometimes apply to one system but not the other, one can expect cross-fertilization – even unexpected discoveries intended for one system but of greater import for the other.

Keith, D.W. 2009. Why capture CO<sub>2</sub> from air?, *Science* **325**, pp. 1654-1655.

Lackner, K.S., S. Brennan, J.M. Matter, A-H. Alissa Park, A. Wright, B. van der Zwaan 2012. "The urgency of the development of CO<sub>2</sub> capture from ambient air," *Proc. Natl. Acad. Sci* **109**, pp. 13156-13162.

Socolow, R., et al., 2011. Direct Air Capture of CO<sub>2</sub> with Chemicals: A Technology Assessment for the APS Committee on Public Affairs, *APS Report*. <http://www.aps.org/policy/reports/assessments/upload/dac2011.pdf>