Accelerating Breakthrough Innovation in Carbon Capture, Utilization, and Storage

Report of the Mission Innovation Carbon Capture, Utilization, and Storage Experts' Workshop

Mission Innovation
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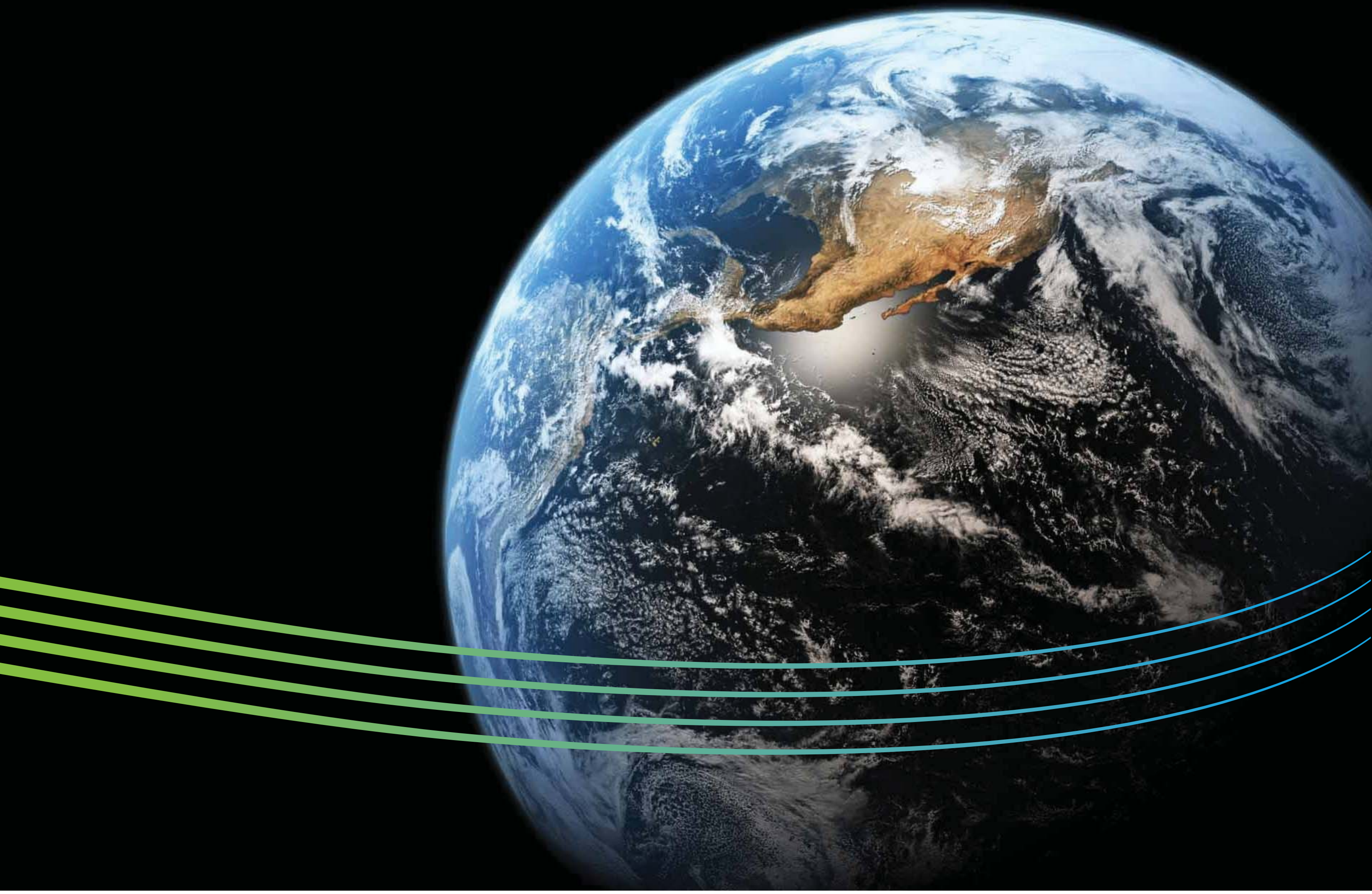

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Ministry of Energy, Industry & Mineral Resources

Disclaimer: This report is the product of the carbon capture, utilization, and storage (CCUS) experts' workshop held in Houston Texas from 26 to 28 of September 2017. The content of this report reflects the views and opinions of the workshop participants and report authors, and does not necessarily reflect those of their respective governments, companies, or academic institutions.

MISSION INNOVATION
Accelerating the Clean Energy Revolution

Carbon Capture Innovation Challenge

Report of the Carbon Capture, Utilization and Storage Experts' Workshop

September 26–28, 2017
Houston, Texas

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Preface

The current global energy system relies on the combustion of fossil fuels to power the world economy. Fossil fuels are used to produce electricity and play a critical role the industrial sector, particularly in the manufacture of cement, fertilizer, and steel. Fossil fuels are expected to play an important role in the future global energy system; however, technical solutions are needed to reduce carbon dioxide (CO_2) emissions from fossil fuel combustion. Carbon capture, utilization, and storage (CCUS) is a key technological approach that can achieve this goal. CCUS is a process that includes the separation of CO_2 from power station or industrial plant effluents, to be used as a feedstock for useful products and/or permanently stored deep underground in geological formations.

The Intergovernmental Panel on Climate Change (IPCC) and other international organizations have concluded that CCUS can play a crucial role in achieving ambitious CO_2 emissions reductions. Many of the major integrated assessment models focusing on 450 ppm scenarios are not able to achieve the needed reductions in global CO_2 emissions without CCUS. According to the IPCC Working Group III Report on Climate Mitigation for the Fifth Assessment Report, the cost of achieving a 450 ppm scenario without CCUS represents a 138% increase compared with a default case that includes CCUS. That is why CCUS is a subject of extensive international research collaborations, investments, and policy developments.

Decarbonizing the power sector has been an important focus of CCUS efforts; however, the application of CCUS technology is also needed for emissions reductions from energy-intensive industries such as cement, steel, chemicals, and many other manufacturing sectors. CCUS is one of the few means of achieving deep emissions reductions in energy-intensive industries, and it can play a key role in balancing intermittent renewable power by providing a low-carbon source of baseload electricity.

Carbon capture, geologic storage, and carbon utilization are all well understood technologies, and successful large-scale integrated projects are already in operation around the globe. Opportunities remain to improve performance, reduce costs, discover new uses for CO_2, and implement regulatory frameworks and international standards to provide certainty in permitting and operation of CCUS projects. The Mission Innovation Carbon Capture Challenge complements international efforts under the Carbon Sequestration Leadership Forum, the Clean Energy Ministerial CCUS Initiative, and other multilateral initiatives focused on CCUS.

The Mission Innovation Carbon Capture Challenge aspires to provide a platform for advancing broad international collaboration in CCUS research and development that could significantly reduce CO_2 emissions from power plants and energy-intensive industries. This report is the collective outcome of the Mission Innovation CCUS Experts workshop, in which an international team worked collaboratively to identify research gaps and opportunities in CCUS. The report identifies research directions that will achieve revolutionary, not just incremental, advances. We hope researchers will draw on the findings of this report to launch collaborative research efforts that accelerate the pace of CCUS innovation.

Contents

Acronyms

1D	one-dimensional
2D	two-dimensional
3D	three dimensional
4D	four dimensional
1×	first generation
2×	second generation
3×	third generation
AFS	advanced flash stripper
AMR	autothermal methane reforming
C1	one-carbon
CaL	calcium looping
CaO	calcium oxide
CAPEX	capital expense
CCS	carbon capture and storage
CCUS	carbon capture, utilization, and storage
CFD	computational fluid dynamics
CLC	chemical looping combustion
CLOU	chemical looping with oxygen uncoupling
CLR	chemical looping reforming
CNF	carbon nanofiber
CO_2	carbon dioxide
CMS	carbon molecular sieve
CPU	CO_2 processing units
DOE	US Department of Energy
EDX	energy-dispersive x-ray
EMR	enhanced metal recovery
EM	electromagnetic
EOR	enhanced oil recovery
FTM	facilitated transport membrane
GDE	gas diffusion electrode
GHG	greenhouse gas
GJ	gigajoule
Gt	gigatonne
HPC	high-performance computing
IEA	International Energy Agency
InSAR	interferometric synthetic aperture radar
ITM	ion transport membrane
LCA	life cycle analysis
LHV	lower heating value
M	magnitude
MCFC	molten carbonate fuel cell
MEA	monoethanolamine
MOF	metal-organic framework

Mt	million tonne
Mtpa	megatonnes per year
NCCC	National Carbon Capture Center
NETL	National Energy Technology Laboratory
NO_x	nitrogen oxide
NRCan	Natural Resources Canada
NWP	numerical weather prediction
OPEX	operating expense
OTM	oxygen transport membrane
PAN	polyacrylonitrile
PM	particulate matter
PRDs	Priority Research Directions
PSA	pressure swing adsorption
PZ	piperazine
R&D	research and development
SEM	scanning electron microscopy
SMR	steam methane reforming
SO_x	sulfur oxide
SWD	saltwater disposal
syngas	synthesis gas
TEA	technoeconomic analysis
TLP	traffic-light protocol
Tpd	ton per day
TR	thermal rearranged polymer
TRL	technology readiness level
TSA	temperature swing adsorption
VSA	vacuum swing adsorption

Executive Summary

Much of the anthropogenic carbon dioxide (CO_2) released into the atmosphere is generated by combustion of fuels for energy production, including fossil-derived fuels (coal, petroleum, and methane and other gases) as well as biomass and bio-derived liquid fuels. The hydrocarbons in these fuels are combusted to provide energy required for transportation (land, air, and sea), as well as to generate electricity and heat used in homes, offices, and industry. As demands for energy have increased globally, CO_2 levels have risen sharply, from pre-industrial levels of 280 ppm a century ago to over 400 ppm since 2013. These levels also include emissions generated from other, nonenergy sources, including steel, aluminum, and cement production; fermentation; chemical production; and other industrial sources. Continued economic and population growth drive the increase in CO_2 emissions; and the levels of emissions, if left unchecked, are projected to exceed 530 ppm by 2100. Goals for stabilizing CO_2 levels at $\leq$450 ppm were set in 2007 to avoid serious impacts to the environment and health [IPCC 2007]. To meet these goals, however, requires substantial improvements in energy efficiency, increased deployment of renewable and nuclear energy, and the development of new technologies for mitigating CO_2 emissions arising from the use of fossil fuels and other anthropogenic sources. [IPCC 2014]

In 2014, the global carbon emissions from fossil-derived fuel combustion were estimated to be 9855 million metric tons of carbon, or nearly 36 gigatonnes (Gt) of CO_2 [Boden et al. 2017]. About a quarter of these emissions come from mobile sources, such as automobiles and other forms of transportation. Much of the remainder comes from point sources—plants used for generation of electricity and heat for industry, business, and home use, as well industrial production processes. It is these so-called point-sources that are the focus of technologies for mitigating global CO_2 emissions.

Among approaches to reducing CO_2 emissions are three processes: carbon capture, utilization, and storage (CCUS). Capture processes are designed to remove and concentrate CO_2 from gas streams in preparation for utilization or storage. Utilization processes are designed to convert CO_2 to higher-value products (e.g., fuels, plastics) or to stable products for long-term storage (e.g., minerals). Storage processes are designed to store CO_2 safely and prevent its reentering the atmosphere. CCUS processes have been deployed at various sites for a number of years, proving that the technologies of capture and storage are commercially available at an industrial scale. Nevertheless, the vast quantities of emissions and the associated costs for CCUS demand that new technologies be developed to make CCUS processes more efficient and economical if the goals for atmospheric CO2 stabilization are to be met.

This report is the product of a workshop that focused on assessing the most promising research avenues for enhancing CCUS processes. Specifically, the goal of the workshop was to assess current gaps in CCUS technologies and identify the most promising directions for basic research (Priority Research Directions, or PRDs) that is needed to achieve long-term global carbon management. These PRDs include opportunities for understanding and improving materials, chemical processes, and other scientific and technical areas required to develop the next-generation technologies needed for efficient, cost-effective management of carbon emissions. Three panels were formed, corresponding to the core topics of Capture, Utilization, and Storage. A fourth panel, Crosscutting, assessed research directions common to the three core topics.

The Capture panel focused both on improvements needed for new processes that will remove CO_2 from gas streams, and on improved combustion processes to reduce CO_2 emissions. Within this panel, four subpanels were formed that addressed Solvents, Sorbents and Looping Systems, Membranes, and Combustion and Other Technologies. The Capture panel focused on developing the in-depth understanding of the myriad of chemical and physical interactions that occur at the interfaces of gases, liquids, and solids. This understanding is a precursor to provide breakthroughs in carbon capture technologies such as solvent-based, sorption-based and membrane-based separation/enrichment of CO_2 effluent streams. In addition, the panel examined next-generation combustion concepts, particularly those conducted at extremes of temperature and pressure, to increase the efficiency of combustion and thus enrich the CO_2 content in the effluent streams to enable cost-efficient CO_2 capture.

The Utilization panel was divided into four subpanels: Thermochemical Conversion and Hydrogenation of CO_2, Electrochemical and Photochemical Conversion of CO_2, CO_2 Permanent Storage of CO_2 in Valuable Products through Carbon Mineralization, and Biological CO_2 Conversion. Electrochemical, photochemical, and biological process, as well as hybrid processes, for conversion of CO_2 provide a particularly compelling vision to produce useful products—materials and chemicals—in an efficient, cost-effective manner. Such processes could provide an economic driver for utilizing CO_2 emissions and could be incorporated synergistically into industrial processes. For example, CO_2 emitted from large-scale industries (e.g., steel, cement) could be converted into additional ethanol via fermentation processes. Chemical conversion processes are also required to use CO_2 to form highly stable materials that can be deployed for long-term geologic storage or for the production of useful materials. This panel also examined energy-lean processes to mineralize CO_2, pointing out that very little is known about the fundamental mechanisms that drive carbon mineralization reactions, particularly near solid–liquid–gas interfaces.

The Storage panel was also divided into four subpanels: Injectivity and Capacity; Monitoring, Verification and Performance Metrics; Forecasting and Managing Induced Seismicity; and Well Integrity. This panel examined the physical and chemical processes that affect CO_2 flow and trapping across vast length and time scales, which can provide greater well stability and capacity. Another area of interest was understanding, and subsequently devising monitoring processes to ensure the success of injection projects, as well as assessing, monitoring, and mitigating potential environmental and safety hazards associated with large-scale injection projects. These hazards include induced seismicity and well degradation that lead to uncontrolled releases of CO_2.

The Crosscutting panel worked with the Capture, Utilization, and Storage panels to assess common themes that cut across these three core areas. All three panels noted that to accelerate materials discovery and process development, close coupling of experiment, computation, and data analytics/machine learning across large temporal and spatial scales are absolutely essential. This effort will also require teams of scientists and engineers from across multiple disciplines to work closely together, bridging basic and applied research, to deliver the knowledge needed to provide the most effective technology solutions. Finally, the Crosscutting panel also considered technoeconomic issues associated with CCUS and assessed how to incorporate social aspects into CCUS decision-making.

As the four technical panels concluded their deliberations, they were charged to identify the most promising research efforts that could be pursued by the international community. These PRDs, listed in Table 1, are not meant to be prescriptive and all-inclusive. Rather, they are designed to inspire multidisciplinary research teams of scientists and engineers from around the globe to elucidate the foundational chemical and physical phenomena that underpin CCUS. With this knowledge, today's technology challenges will be overcome, current technologies will be improved, and a new generation of CCUS technologies will be catalyzed. These PRDs will yield the design of new materials, novel chemical and physical processes, and new sensors and characterization and computational tools that will make CCUS processes more efficient, reliable, and cost-effective. The workshop participants acknowledged that the challenges of CCUS are daunting, but they were confident that research addressing the identified PRDs holds enormous promise for reaching the goal of stabilizing global CO_2 levels.

The technologies needed to make CCUS work on an industrial scale are commercially available today, as is demonstrated by CCUS processes that have been deployed at various sites for a number of years. The PRDs described in this report will guide the R&D that will be required to improve current technologies to deliver CCUS at the scale that is expected to be needed in the period 2030–2050.

Table 1. Priority Research Directions

Capture
Designing high-performing solvents for CO_2 Capture
Creating environmentally friendly solvent processes for CO_2 capture
Designing tailor-made sorbent materials
Integrating sorbent materials and processes
Understanding transport phenomena in membrane materials
Designing membrane system architectures
Catapulting combustion into the future
Producing hydrogen from fossil fuels with CO_2 capture
Utilization
Designing complex interfaces for enhancing hydrocarbon recovery with carbon storage
Valorizing CO_2 by breakthrough catalytic transformations into fuels and chemicals
Creating new routes to carbon-based functional materials from CO_2
Designing and controlling molecular-scale interactions for electrochemical and photochemical conversion of CO_2
Harnessing multiscale phenomena for high-performance electrochemical and photochemical transformation of CO_2
Accelerating carbon mineralization by harnessing the complexity of solid–liquid interfaces
Tailoring materials properties to enable carbon storage in products
Tailoring microbial and bioinspired approaches to CO_2 conversion
Hybridizing electrochemical and biological process for CO_2 conversion to fuels, chemical, and nutrients
Storage
Advancing multiphysics and multiscale fluid flow to achieve gigatonne/year capacity
Understanding dynamic pressure limits for gigatonne-scale CO_2 injection
Optimizing injection of CO_2 by control of the near-well environment
Developing smart convergence monitoring to demonstrate containment and enable storage site closure
Realizing smart monitoring to assess anomalies and provide assurance
Improving characterization of fault and fracture systems
Achieving next-generation seismic risk forecasting
Locating, evaluating, and remediating existing and abandoned wells
Establishing, demonstrating and forecasting well integrity
Crosscutting
Integrating experiment, simulation, and machine learning across multiple length scales to guide materials discovery and process development
Coupling basic science and engineering for intensified carbon capture, purification, transport, utilization and storage processes
Incorporating social aspects into decision-making
Developing tools to integrate life-cycle technoeconomic, environmental, and social considerations to guide technology portfolio optimization

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1. Introduction

There is general consensus that global energy demand will continue to rise, driven primarily by continued increases in both population and economic growth. At the same time, climate change from increased levels of carbon dioxide (CO_2) released into the atmosphere has become a top international priority. Consequently, more energy will have to be delivered, but with far less emissions, to meet the international commitment to limit the increase in average Earth temperature well below 2°C compared with pre-industrial temperatures.[1]

Over the past decades, innovation and technology have enabled global prosperity, improved quality of life, and enhanced energy security. Innovation in clean energy technologies holds the answer to the energy and climate challenges. However, with the addition of two billion energy consumers over the next decades,[2] a step change in innovation is required to make clean energy widely available and affordable globally.

Mission Innovation recognizes that a boost in clean energy innovation is critical for achieving global climate targets. Unveiled in November 2015 at the United Nations 21st Conference of the Parties (COP21) in Paris, Mission Innovation is a global initiative of 22 countries and the European Commission representing more than 80% of the world's total public investment in clean energy research and development (R&D), 60% of world population, 70% of global gross domestic product, and 67% of total greenhouse gas emissions. As a Ministerial level initiative, the goal of Mission Innovation is to accelerate the pace of clean energy innovation so as to achieve performance breakthroughs and cost reductions that can deliver widely affordable and reliable clean energy solutions across the world in the next two decades and beyond. The initiative seeks to double governmental investment in clean energy innovation, increase private sector engagement in clean energy innovation, and improve information sharing among Mission Innovation countries.

In December 2016 at the COP22 in Marrakech, seven innovation challenges were launched as global calls to action aimed at catalyzing global research efforts in areas that could provide significant benefits in reducing greenhouse gas emissions, increasing energy access and security, and creating new opportunities for clean economic growth. The seven innovation challenges cover a broad spectrum of clean energy technologies such as the following:

- **Smart Grids Innovation Challenge**—to enable future grids that are powered by affordable, reliable, decentralized renewable electricity systems
- **Off-Grid Access to Electricity Innovation Challenge**—to develop systems that enable off-grid households and communities to access affordable and reliable renewable electricity
- **Carbon Capture Innovation Challenge**—to enable near-zero CO_2 emissions from power plants and carbon-intensive industries
- **Sustainable Biofuels Innovation Challenge**—to develop ways to produce, at scale, widely affordable, advanced biofuels for transportation and industrial applications
- **Converting Sunlight Innovation Challenge**—to discover affordable ways to convert sunlight into storable solar fuels
- **Clean Energy Materials Innovation Challenge**—to accelerate the exploration, discovery, and use of new high-performance, low-cost clean energy materials
- **Affordable Heating and Cooling of Buildings Innovation Challenge**—to make low-carbon heating and cooling affordable for everyone

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[1] United Nations Framework Convention on Climate Change Paris Agreement, http://unfccc.int/2860.php. Accessed April 2018.

[2] International Energy Agency, 2016 World Energy Outlook. Available at https://www.iea.org/newsroom/news/2016/november/world-energy-outlook-2016.html. Accessed April 2018.

Work under each the Innovation Challenges is guided by four collective objectives:

1. Building an improved and shared understanding of what is needed to address each Challenge and of how to define measurable targets and track progress toward them
2. Identifying key gaps and opportunities not sufficiently addressed by current activities
3. Promoting opportunities for researchers, innovators, and investors in order to build support and excitement around the Challenges and boost engagement
4. Strengthening and expanding collaboration among key partners, including governments, researchers, innovators, and private sector stakeholders

The Carbon Capture Innovation Challenge is one of the seven Mission Innovation challenges. It has participation from about 20 countries, which underscores the importance of CO_2 capture, utilization, and storage (CCUS) for clean energy innovation. Much of the CO_2 is released into the atmosphere when fossil fuels (coal, petroleum, and natural gas), as well as biomass and bio-derived fuels, are directly combusted, transformed to other energy forms, or used in industry. The transformation includes fuels for transportation (land, air, and sea), as well as generation of electricity and heat used in homes, offices, and industry. As demands for energy have increased globally, CO_2 levels have risen sharply, from pre-industrial levels of 280 ppm a century ago to over 400 ppm since 2013. These levels also include emissions generated from other, nonenergy sources, including steel, aluminum, and cement production; fermentation; chemical production; and other industrial sources. Continued economic and population growth drive the increase in CO_2 emissions; and the levels of emissions, if left unchecked, are projected to exceed 530 ppm by 2100. Goals for stabilizing CO_2 levels at $\leq$450 ppm were set in 2007 to avoid serious impacts to the environment and health [IPCC 2007].

The Carbon Sequestration Leadership Forum (CSLF) recognizes CCUS as a key technology to reduce CO_2 emissions across various sectors of the economy while providing other societal benefits such as energy security and access, air pollution reduction, grid stability, and job preservation and creation.[3] The Clean Energy Ministerial (CEM) similarly recognizes the need for a comprehensive climate change policy, one that will require CCUS technologies to enable global carbon reductions.

The Carbon Capture Challenge seeks to enable near-zero CO_2 emissions from power plants and carbon-intensive industries. The Challenge focuses on research, as opposed to deployment and/or policy issues, to avoid duplication of efforts with others multilateral initiatives such as the CSLF and the CEM.

Under the co-leadership of the United States of America and the Kingdom of Saudi Arabia, the Carbon Capture Innovation Challenge organized an international workshop on CCUS to discuss basic research needs and breakthrough ideas centered on four focus areas: CO_2 capture, CO_2 utilization, CO_2 storage, and crosscutting CCUS topics. Each of the four focus areas was composed of panels of participants from universities, industries, and national laboratories, covering a broad range of expertise. These specially selected participants represented world-leading scientists who focused on defining the fundamental science needs to address the most critical scientific challenges in CCUS.

This report comprises the findings from the four workshop focus areas. It contains the corresponding four main chapters describing the current status of CCUS technologies, major scientific challenges, and recommendations for priority research directions (PRDs) that have the potential to make significant impacts in improving CCUS technology performance. Section 2 addresses issues related to CO_2 capture technologies, with particular focus on solvents, sorbents, membranes, and combustion and other capture technologies. Chapter 3 addresses CO_2 utilization technologies, focusing on thermochemical conversion and hydrogenation; electrochemical and photochemical conversion; biological conversion; and conversion to solid carbonates. Chapter 4 addresses scientific issues related to CO_2 storage, focusing on

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[3] Carbon Sequestration Leadership Forum *2017 Carbon Sequestration Technology Roadmap*. Available at https://www.cslforum.org/cslf/sites/default/files/2017CSLFTechnologyRoadmap.pdf. Accessed April 2018.

injectivity and capacity; monitoring; verification and performance metrics; forecasting and managing induced seismicity; and well diagnostics. Chapter 5 discusses crosscutting topics that are relevant to at least two of the three CCUS technologies; it covers technoeconomic assessment, life cycle analysis, and inclusion of social aspects in CCUS technology development.

In each focus area, a number of PRDs were generated. These PRDs were formulated to represent the most promising basic research areas with the potential to provide breakthroughs needed to meet future clean energy goals. They are meant to inspire the international CCUS research community, governments, and the private sector, helping to guide national R&D investments and programs.

The technologies that are needed to make CCUS work on an industrial scale are commercially available today, as is demonstrated by CCUS processes that have been deployed at various sites for a number of years. The PRDs described in this report will guide the R&D that will be required to improve current technologies to deliver CCUS at the scale that is expected to be needed in the period 2030–2050.

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2. Carbon Dioxide Capture

Fossil-derived hydrocarbons are used globally for power and heat production, as well as in a broad range of global industrial processes, such as steel, cement, and hydrogen production, natural gas cleaning, and chemicals production. Together, these processes emit gigatonnes of CO_2 annually. Unlike the power sector, where alternative power sources are becoming more broadly available, industrial processes have limited options for substituting fossil feedstocks to reduce emissions. In addition, some industrial processes, such as cement production, emit CO_2 when processing raw materials. Thus, the application of carbon capture and storage to industrial processes will be critically important even if alternative power production sources are broadly utilized.

Traditionally CO_2 capture has been classified in three main areas (Figure 2.1):

- capturing CO_2 after combustion (post-combustion)
- burning the fuel in relatively pure oxygen to facilitate capture (oxy-combustion)
- converting a fossil feedstock to CO_2 and H_2 and separating these gases before combustion (pre-combustion)

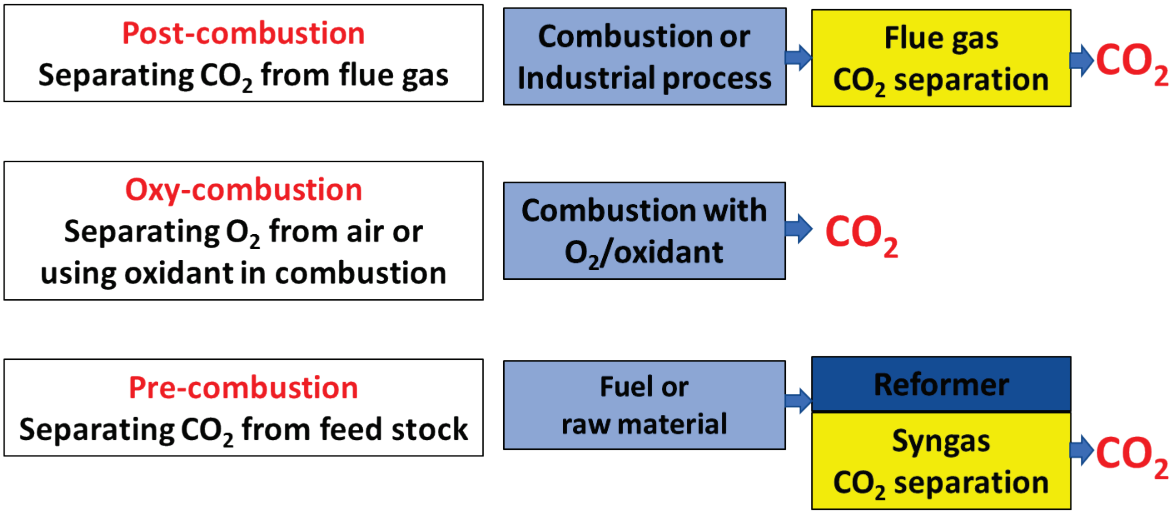

Figure 2.1. Three pathways for CO_2 capture. | Image courtesy of Gassnova SF

Some commonly used strategies to capture/separate gases include solvents for absorption and solid sorbents for adsorption/absorption, as well as membranes and cryogenic processes for separation. These various approaches for separating gases are used for all types of capture processes--pre-combustion, oxy-combustion, and post-combustion. For example, both solvents and membranes are used in both pre- and post-combustion.

Capturing the CO_2 from power and industrial sources requires highly efficient separation processes. Today's technologies face common challenges, including robust materials, gas selectivity, capacity, efficiency, footprint, and cost of the whole capture process, including utilities and support systems.

Based on the major research areas for CO_2-capture, the following panels were defined:

- C1—Solvents: Research in novel types such as nonaqueous, two-phase, and phase-changing solvents, as well as improvement of existing ones.
- C2—Sorbents: Research in sorbents for chemical/carbonate looping; sorption-enhanced shift, reforming, and swing processes; and adsorbents.

- C3—Membranes: Research in polymeric, hybrid, carbon, metallic, and ceramic membranes and various types of composite and dual-phase membranes
- C4—Combustion: Research in combustion and other technologies that do not fit easily into any of the other three categories.

Even though the panels considered different separation techniques and fields of research, they recognized there are overlapping areas among all of them. For example, chemical looping combustion could have been under panel C4 rather than panel C2, and metal-organic frameworks are mentioned by both panels C2 and C3.

The Mission Innovation CCUS workshop focused on technology readiness levels (TRL) 1 to 3 (4). For the Capture Focus Area, this meant laboratory-scale research activities and analytical and modeling work, i.e., mainly fundamental research. As guidance for the types of R&D activities to be conducted, Table 2.1 presents a short version of a combination of definitions used by EU Horizon 2020,[1] the US Department of Energy (DOE),[2] and Natural Resources Canada (NRCan)[3] for research activities at TRL 1–4.

Table 2.1. Combination of EU H2020 TRL summaries and DOE and NRCan detailed descriptions for maturity levels

TRL	Definition	Description of research activities
1	Basic principles observed	Early-stage scientific research begins the translation to applied RD
2	Technology concept formulated	Technology development begins—once basic principles are observed, development of practical and specific applications can be initiated
3	Experimental proof of concept	Active R&D is initiated to establish proof of concept, including analytical and laboratory studies to physically validate analytical predictions of separate elements of the technology
4	Technology validated in laboratory	Basic technological components are integrated to establish that the pieces will work together

Today, the major general gas separation processes that are commercially available are used in applications in which the product has a commercial value (e.g., CO_2 in the food industry, oxygen and hydrogen for various uses). However, CCUS will require steps in addition to gas separation—steps that increase costs. Despite some early examples of CO_2 capture for large-scale CCUS,[4] research must seek improvements in the overall production costs of CCUS through factors such as reduced investments (capital expenditures—CAPEX) and operational expenses (OPEX), including parasitic energy. Thus, CCUS processes need to be designed and optimized holistically as a highly integrated system.

Currently, solvent-based capture processes, particularly amine-based capture, are more mature than sorbent- or membrane-based technologies and have reached their present level of technology readiness and commercialization because the *whole* process system has been developed and continuously improved over decades. Novel technologies that are developed must offer potential advantages over future improved versions of the incumbent technologies (e.g., amines) to be attractive. To this end, they must

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[1] http://ec.europa.eu/research/participants/data/ref/h2020/other/wp/2016-2017/annexes/h2020-wp1617-annex-ga_en.pdf

[2] http://www2.lbl.gov/dir/assets/docs/TRL%20guide.pdf

[3] https://www.nrcan.gc.ca/energy/science/programs-funding/eip/20024

[4] In the power sector, the largest examples are Boundary Dam in Canada and Petra Nova in the USA. Several industrial plants have implemented carbon capture and storage, including Quest in Canada, (hydrogen production), the Emirates Steel Industry in the United Arab Emirates, the Illinois Industrial Project in the USA, and the Tomakomai refinery in Japan. The Global Carbon Capture and Storage Institute [GCCSI 2016a, 2016b] gives more extensive reviews of implemented CCUS projects in the power and industry sectors.

improve not only the core technology (e.g., sorbent or membrane) but also the whole system. Therefore, other considerations than just energy efficiency and product cost may come into play, e.g., environmental considerations, footprint (dimensions and weight), and infrastructure. Testing facilities and improved models to elevate lower-TRL opportunities are needed.

Advances in carbon capture will build not only on fundamental research in this area, but also on cumulative gains from many research fields that result in synergistic effects. In their discussions and identification of PRDs, the Capture Focus Area panels acknowledged this overlap by considering the following topics:

- Advanced manufacturing systems (3D/4D printing opens new possibilities).
- Process intensification and integration (reduced sizes, new equipment and process configurations). Linked to a variety of material choices and additive manufacturing, this field could pave the way for game-changing solutions.
- Materials discovery.
- System design for improved energy efficiency and lower cost.
- Targeted application improvements (e.g., heat integration, reactors, improved kinetics, industrial applications).
- Environmental issues, including water consumption.

Because of the decision to focus on low-TRL areas, the panels concentrated on fundamental research and did not include these aspects of technology development directly as PRDs.

The PRDs are designed to inspire multidisciplinary research teams of scientists and engineers. The aim is to develop more in-depth understanding of chemical and physical interactions at the interfaces of gases, liquids, and solids at the molecular level. Doing so will spur the development of materials and processes that could pave the way to new systems for separating CO_2, H_2, O_2, and other gases efficiently, in an environmentally friendly manner, and at affordable cost. Pursuing these PRDs will enable improved understanding of material properties, new materials, and new chemical and physical processes that take advantage of molecular-level interactions. The eight PRDs developed as part of the Capture theme areas are

C-1: Designing High-Performing Solvents for CO_2 Capture
C-2: Creating Environmentally Friendly Solvent Processes for CO_2 Capture
C-3: Designing Tailor-made Sorbent Materials
C-4: Integrating Sorbent Materials and Processes
C-5: Understanding Transport Phenomena in Membrane Materials
C-6: Designing Membrane System Architectures
C-7: Catapulting Combustion into the Future
C-8: Producing Hydrogen from Fossil Fuels with CO_2 Capture

2.1 Capture Panel Report: Solvents

Carbon capture by solvents requires the design of high-performance solvent systems, mitigation of solvent loss and environmental impacts, and intensification of processes. The ideal process must both capture the targeted gas and release it efficiently to regenerate the solvent for subsequent use with low energy requirements. The research needs identified for solvent capture processes arise from the current state- of-the-art second-generation amine processes and of third-generation water-lean and multiphase solvents. Increased research in these areas will bridge knowledge gaps and enable the deployment of CCUS by discovering improved solvents, accelerating maturation, enhancing performance, and reducing risk, cost, and environmental impacts. The importance of applying technologies across a broad spectrum of CCUS applications must be recognized.

2.1.1 Status of Solvent-Based Technologies

Second-generation amine scrubbing

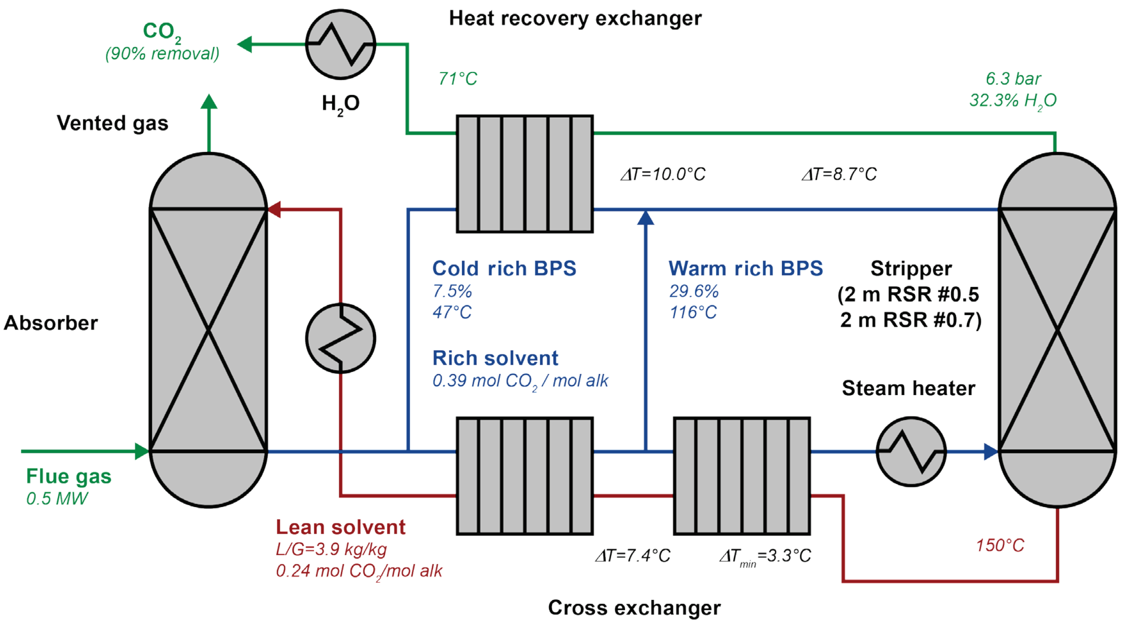
Amine scrubbing has been used since 1930 to remove H_2S and CO_2 from natural gas. Its use on flue gas for CO_2 capture started in 1980 with the solvent monoethanolamine (MEA). Amine scrubbing was identified as the technology of choice for CO_2 capture around the year 1990. It is still the technology of choice, and future generations of amines and advanced solvents may well maintain this position. Second-generation amines and processes have been developed by more than ten companies and organizations. The sidebar “Example of Second-Generation Solvent Process” presents a typical example of the process.

Two amine scrubbing systems have been commercialized at coal-fired power plants. The MHI solvent KS-1 with an “energy saving process” and the Cansolv solvent DC-103, with lean vapor compression, are operating near design conditions with a reboiler heat duty of 2.3–2.4 GJ/tonne CO_2 removed [Rochelle 2014], compared with 3.5 GJ/tonne [DOE/NETL 2007] for first-generation amine scrubbing.

The thermodynamic efficiency of second-generation amine scrubbing is ~50%. The ideal work requirement to separate CO_2 from coal-fired flue gas and compress it to 150 bar is 110 kwh/tonne CO_2. The Cansolv and MHI commercial units are operating with an estimated total electricity burden (including heat) of 220–240 kwh/tonne CO_2 removed. A reversibility analysis of aqueous piperazine (PZ) with an advanced flash stripper (AFS) shows that this typical second-generation system requires 230 kwh/tonne (see Figure 2.2). The irreversibility of this system is distributed among several unit operations, so there is no easy means of improving second-generation amine scrubbing.

In summary, energy improvements have achieved an equivalent electricity requirement of close to 230 kwh/tonne CO_2 at >50% thermodynamic efficiency for second-generation amine scrubbing; improvement opportunities are limited by the ideal work requirement. It should be emphasized that, in cases of implementation of CS in energy-intensive industries like cement and steel, solvent regeneration may in some cases make use of excess heat. This shows the significant benefit of heat-driven separation processes. If steam must be derived from a separate boiler, parameters related to primary energy usage or cost would be a more appropriate performance indicator than the equivalent electricity requirement. Remaining challenges to address are oxidation and amine aerosol research to eliminate uncertainty.

Example of Second-Generation Solvent Process



Piperazine with an advanced flash stripper. | Image courtesy of G. T. Rochelle, University of Texas–Austin

In this example of a second-generation amine scrubbing process, 30 wt. % piperazine is fed into the top of the absorber. In advanced regeneration, the rich solvent containing dissolved CO_2 is fed from the bottom of the absorber through two heat exchangers and a steam heater to the bottom of the stripper at 150°C and elevated pressure. Two slipstreams of the rich solvent are fed to the top of the stripper. As it passes through the stripper, the vapor from the bottom of the stripper removes the dissolved CO_2 from the rich solvent. The vapor is cooled to produce pure CO_2, which is sent to the compressor for further use in the CCUS process.

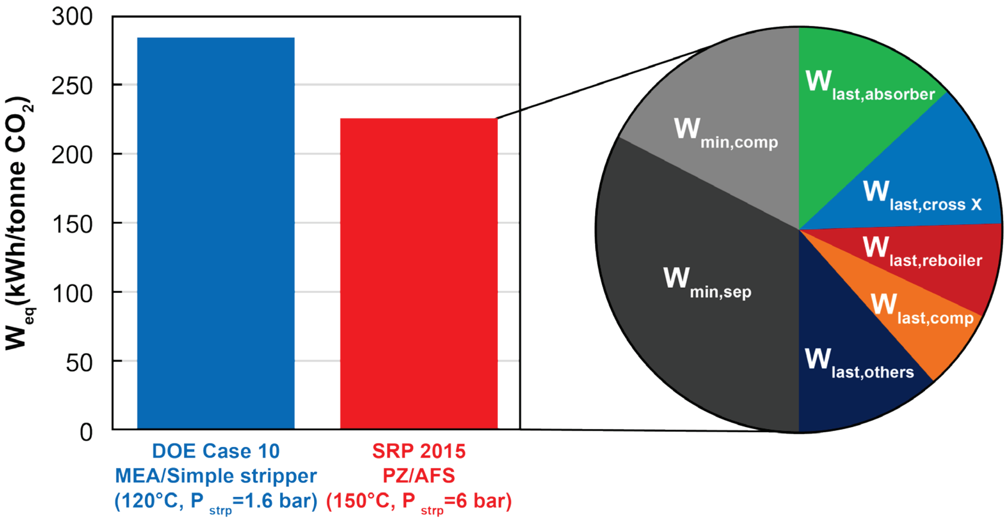


Figure 2.2. Example showing that second-generation amine scrubbing provides 50% thermodynamic efficiency with 20% less work than first-generation MEA. | Reproduced from Lin, Y-J, E. Chen, and G. T. Rochelle. 2016. "Pilot plant test of the advanced flash stripper for CO_2 capture." *Faraday Discussions* **192**, 37–58, with permission of The Royal Society of Chemistry.

Water-lean solvents

Water-lean solvent systems are solvent processes that retain the chemical selectivity of water-based solvents. The goal is to reduce the energy required to regenerate the solvent by exploiting the lower specific heats of organics compared with that of water. Most of these third-generation solvents are in the early stages of development (TRL 1–4), and measurements of rudimentary data to enable accurate performance modeling for progression to larger-scale testing and adaptation are still under way. From a time and cost perspective, these solvents have the potential to use first- and second-generation aqueous amine infrastructure, enabling a potential rapid ascent up the development ladder.

There are dozens of reported water-lean solvents. However, regardless of formulation, all use one of the three known CO_2 binding chemistries: carbamate, alkylcarbonate, and azoline-carboxylate (Figure 2.3). All reported formulations are nonvolatile by design to minimize fugitive emissions and lessen environmental impacts. Water-lean solvents have enthalpies of CO_2 absorption that are comparable to those of aqueous solvents, ranging from –50 to –90 kJ/mol CO_2, indicating similar selectivity and viability for post-combustion CO_2 capture.

Many water-lean solvents have unique properties that can be exploited for efficiency gains Water-lean solvents exhibit unique physical and thermodynamic properties—such as physical state (e.g., solid, liquid), contact angle, wettability, viscosity and volatility, and thermodynamic properties—such as thermal conductance and solvation free energy—that differ substantially from those of aqueous solvents. Some properties may be detrimental to CO_2 capture performance (e.g., higher viscosity and lower thermal conductance), whereas the lower specific heat and higher physical solubility of CO_2 are beneficial. Other unique solvent behaviors have been discovered, including a higher rate of mass transfer than aqueous solvents, an inverse temperature dependence (a solvent absorbs faster the colder it gets), phase changes (e.g., the ability to concentrate CO_2-containing material to regenerate), and the ability to destabilize the CO_2 carrier (resulting in a reduction in the temperature needed for CO_2 release). In each case, these properties may be exploited to improve process efficiency.

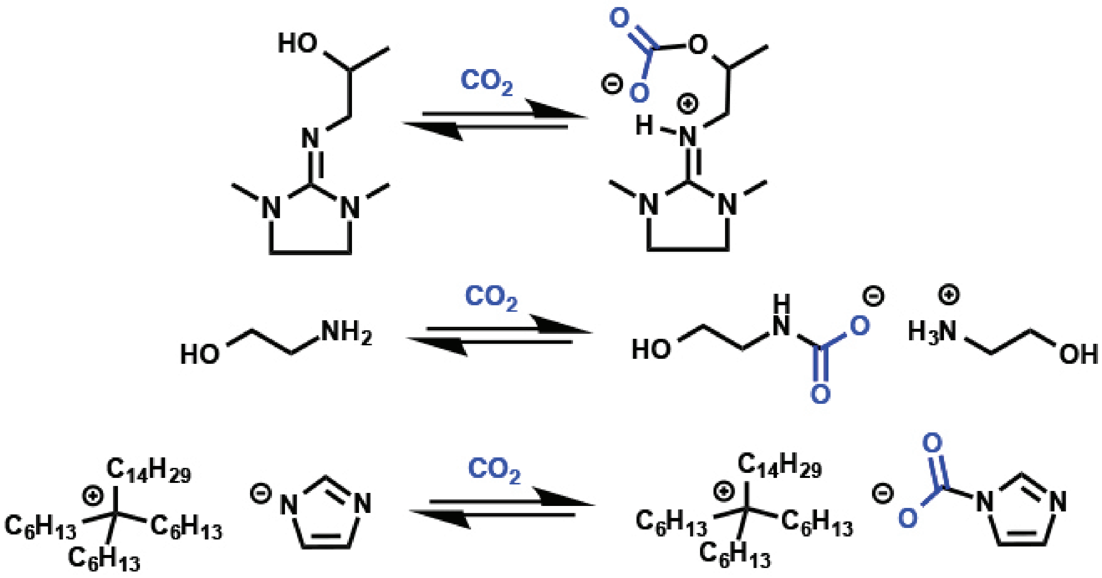


Figure 2.3. Binding mechanisms of CO_2. | Image courtesy of Pacific Northwest National Laboratory

Notable water-lean solvents have reported significant reductions in reboiler duty, from 1.7 to 2.6 GJ/tonne CO_2, compared with the US DOE NETL Case 10 baseline (3.5 GJ/tonne CO_2) or the performance of second-generation amine scrubbing (2.2–2.4 GJ/tonne). The combination of lower reboiler duties and regeneration temperatures below 100°C enable higher plant efficiencies, translating into projections of a 2.1–7.1% increase in net plant efficiency compared with the NETL Case 10 baseline. Costs have been reported to be as low as $39/tonne CO_2 captured, primarily using the first-generation amine infrastructure [Heldebrant et al. 2017]. There is potential for further efficiency gains with second-generation amine infrastructure (e.g., AFSs), in addition to novel configurations that are designed and optimized for the physical and thermodynamic properties unique to these solvents.

Most water-lean solvents have demonstrated an acceptable level of water tolerance, and all solvents report a steady-state loading of water (up to 10 wt %) without a need for exotic water management infrastructure. There are no published reports of aerosols or foaming, an advantage that is hypothesized to be due to the reduced surface tension of organics compared with water. Water-lean solvents may be less corrosive than aqueous solvents. Some amines and amidines have been shown to act as corrosion inhibitors. Additionally, their lower water content reduces the amount of carbonic acid in solution, as carbonic acid is the primary culprit of steel corrosion. A reduced corrosion rate may enable the use of cheaper alloys of steel in process infrastructure, potentially reducing costs.

Water-lean solvents are expected to be roughly as durable against flue gas impurities as their aqueous counterparts, as they both entail the same functional groups, and the amount of the impurities is fixed by the flow rate of flue gas. It has been shown that some acidic gases such as SO_2 could be thermally removed from solution because of their lower acidity in organic solvents than in water, although there are no reported studies on nitrogen oxides (NOx). Finally, oxygen is known to be more soluble in organic liquids, but the rate of oxidation may actually be lower because the solvent regeneration occurs at temperatures significantly below those of aqueous amines.

Multiphase solvents

Multiphase solvents for CO_2 capture consist of solvent systems capable of forming more than one liquid phase (demixing solvents) or liquid/solid systems (precipitating solvents). Phase change as part of an absorption/desorption cycle opens a range of opportunities for improved performance of the capture process:

- Formation of a high-density CO_2-rich phase so that only a part of the solvent requires regeneration. An extremely concentrated phase with high reactant and CO_2 concentration may enable significantly reduced heat requirements in terms of both sensible heat and steam requirements for CO_2 stripping. The low-density phase can contain practically no CO_2 and is recycled to the absorber, whereas all of the CO_2 is present in the high-density phase.
- Intensified desorption at lower temperatures (<100°C), using low-value heat from waste streams.
- High-pressure desorption due to an extreme CO_2 backpressure from the concentrated solvent, enabling a significant reduction in the CO_2 compression cost.
- Precipitation of bound CO_2, or the reactant itself enabling a buildup of bound CO_2 at constant equilibrium pressure, and/or a Le Chatelier shift of equilibria to favor a high loading capacity.

The systems currently under development most commonly perform as one homogeneous liquid phase in the absorber section; whereas a phase change or immiscibility occurs as a result of salt solubility limits, or of the immiscibility of hydrophobic/lipophilic amines or other reactants with limited solubility in the base solvent. Systems with combinations of amines, inorganic salts, organic solvents, and water are being studied for this purpose (Figure 2.4). Several of these solvent process concepts have been studied only recently (during the past 5 years) and have shown a potential for reduced energy requirements and improved performance. There is also a close relationship with and significant potential to use multiphase effects in recently developed nonaqueous/water-lean solvent systems.

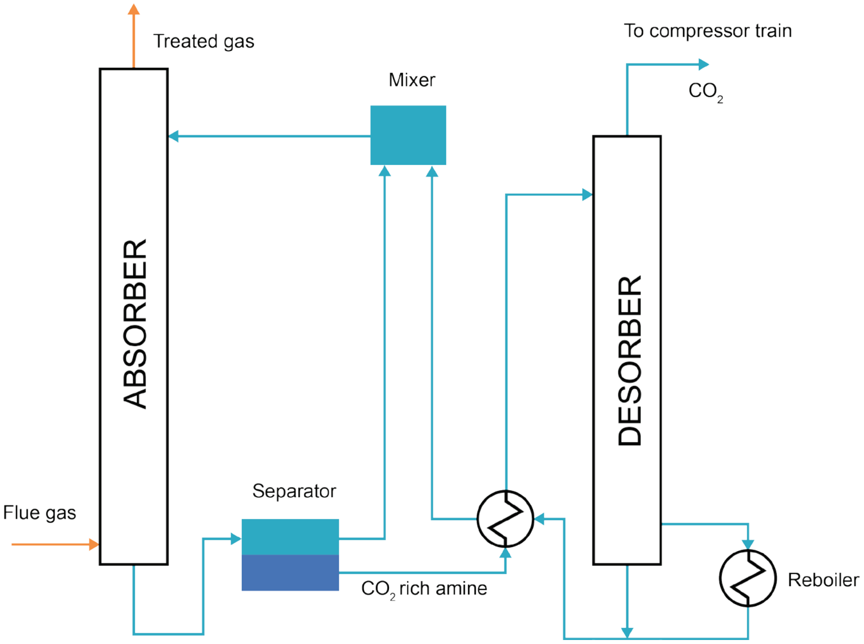


Figure 2.4. Conceptual 2-phase solvent process flow diagram. | Image courtesy of SINTEF

2.1.2 Scientific Challenges

Designing high-performing solvents for CO_2 capture

First- and second-generation aqueous amine systems for CO_2 capture have been successfully engineered over the past several decades to the point that they require only about 2.5 GJ of energy to capture a ton of CO_2. Nonetheless, the capture cost is still roughly \$50–60/ton; and capital cost, operating costs related to solvent cost, corrosion, degradation, volatility, aerosols, and the capture plant footprint remain major issues. If major improvements are to be achieved, there must be significant improvements to the solvents and the related process features, which may differ for different solvent systems.

The research challenge in designing high-performance solvent systems is mastering the ability to accurately predict the chemical and physical properties of potential liquid absorbents for CO_2 capture based on fundamental molecular understanding. The exact properties of an ideal solvent will vary from one application to the next (e.g., post-combustion capture from a pulverized coal plant vs. CO_2 removal from cement manufacturing). Solvent development needs to be integrated with process development. Modeling and simulation can be used to determine the necessary chemical and physical properties. Then the challenge is to design new solvents and solvent mixtures with the necessary property combinations to result in high-performance CO_2 capture systems. Molecular modeling and simulation tools have advanced rapidly, so that it is now possible to design both nonreactive and reactive absorbents from fundamental molecular principles.

Solvent-based CO_2 capture requires large equipment and is capital intensive. The technology is readily available for commercial deployment, yet there is significant potential for capital cost reduction. Capital costs account for up to 50% of total project expenditures. The absorber can represent 50% of total capital costs, and the stripper up to 20%. Reducing the size and/or cost of these units could, therefore, positively impact deployment by significantly reducing costs. Process intensification is an area of chemical engineering focused on developing strategies to dramatically reduce the sizes of existing processes (see the sidebar "Process Intensification."

Process Intensification—An important Research Direction for CAPEX reduction

Scientific challenges

The development of absorption processes for CO_2 capture requires a close interplay between the design of the solvent itself and the process configuration. The topic of process intensification in this context may allow step-change cost reduction that have relevance for all solvents. Next-generation solvents, such as multiphase or water-lean systems, might enable such step-changes to units in the process.

Process intensification can be applied to deliver a step change in costs by

- Increasing mass transfer and reducing the packing height by the use of improved gas–liquid contactors and innovative packing
- Increasing heat transfer and reducing solvent stripper residence time with new stripper concepts
- Reducing costs by eliminating the use of packed contactors
- Lowering construction costs with lower-cost materials (enabled by new solvents or advanced manufacturing)
- Advancing process heat integration tailored to applications
- Reducing the size and the amount of process equipment by integrating flue gas conditioning
- Sharing of infrastructure and subcomponents in CCSU clusters
- Allowing for more modular and/or prefabricated construction and/or field fabrication

There are also huge benefits in footprint reduction and visual impact, which may remove barriers to deployment for retrofitting and permitting in some jurisdictions.

Research direction

- Understanding application-specific challenges
- Developing innovative packing
- Developing contactor-integrated feed gas conditioning that requires no packaging
- Achieving a step-change in corrosion management
- Advancing heat exchanger concepts
- Combining capture and utilization

Major improvements in first- and second-generation aqueous amine systems for CO_2 capture require significant improvement of both solvents and the associated processes, which may differ from one system to another. Solvent development process development must be integrated. Modeling and simulation tools are sufficiently advanced to enable the design of new solvents based on fundamental molecular principles. Process intensification could reduce the size and thus the cost of process equipment.

Creating environmentally friendly solvent processes for CO_2 capture

Three important challenges have been identified for second-generation amine scrubbing that results in amine loss. These are critical to secondary environmental impacts and to the cost of amine makeup and reclaiming.

- **Amine oxidation**. Amine oxidation is a complex problem with many uncertainties. It is critical to the secondary environmental impact and to the cost of amine makeup and reclamation. MEA, KS-1, and DC-103 are being used without insurmountable effects of solvent oxidation. Second-generation solvents such as piperazine, KS-1, and DC-103 are resistant to oxidation; but oxidation still occurs at levels that are problematic. Another challenge is that bench-scale experiments do not yet simulate full-scale experience; O_2 mass transfer often limits bench-scale experiments. Oxidation of mature amine inventory appears to be different from clean solvent. The oxidation rate and the concentration of dissolved iron (an oxidation catalyst) increase with degradation product accumulation. Therefore, continuous reclaiming may reduce oxidation. As both dissolved and entrained O_2 oxidize amines, any foaming may accelerate oxidation. Nitrogen-2 or other stripping/chelation of O_2 may reduce the rate of oxidation. Oxidation occurs in the stripper sump without dissolved O_2; therefore, minimum stripper sump temperature and hold-up may reduce oxidation. The rate of oxidation increases with increasing temperature; thus, any reductions in reboiler temperature may reduce the rate of oxidation.
- **Amine aerosols**. Sulfur trioxide, fine ash, SO_2, and other nuclei in flue gas result in emissions of amine aerosols from second-generation systems. Sulfur trioxide can be eliminated by bag filters or gas–gas heat exchange. Episodal, unknown nuclei may be problematic. The severity of the amine aerosols will probably vary with amine volatility. MHI, Aker Solutions, and others claim to mitigate aerosols with a variety of process features.
- **Nitrosamine**. Nitrogen dioxide in inlet flue gas oxidizes all amines. Secondary amines react to produce carcinogenic nitrosamine, and nitrosamine can thermally degrade, resulting in oxidized amine products. Currently, NO_2 can be effectively minimized by selective catalytic reduction, scrubbing in an SO_2 polisher, or by the use of a bag filter with carbon injection. Other third-generation solvent systems may not use simple amine functions as second-generation systems do, so it remains unknown what mode of nitrosation or oxidation (if any) would be observed.

2.1.3 Why Now?

Solvent-based systems and processes for CO_2 capture are recognized as some of the most ready-to-deploy capture technologies and have received significant research attention. Second-generation amine-based systems are now beginning to be deployed in large-scale demonstration projects, for example, at Boundary Dam, Quest, and Petra Nova. The scale-up of these systems offers unique insight into what outstanding challenges still require attention and how appropriate the bench-scale and pilot-scale testing has been in characterizing how the solvents will perform at scale. The areas of most concern are oxidation, foaming, aerosol formation, and corrosion. As the demonstration projects continue to operate, further insight will be gained regarding other challenges. Operational experience at demonstration scale also offers the opportunity for bench- and pilot-scale facilities to be recalibrated to better represent operation at scale. To enhance fundamental understanding of these operational challenges, sustained research is necessary to improve the underpinning theory and bench- and pilot-scale facilities.

Second-generation solvent systems offer limited opportunities for significant cost reductions or potential for breakthroughs that will enable large-scale deployment at an acceptable cost. Current solvent-based systems are further disadvantaged by improvements in the costs of technologies such as solar power and battery technology. Hence, there is a requirement for new solvent chemistries or processes that cut costs by improving performance, mitigating the energy penalty, or overcoming some of the engineering challenges of second-generation solvent systems. Fortuitously, the lessons learned from the development of current solvent systems and rapid improvements in modeling capability offer opportunities to develop the necessary tools to enhance the design and development of new high-performing solvent systems. These tools and the enhanced learning on the bench- and pilot-scale facilities will better quantify their performance and speed up the time to market. These improvements in fundamental theory, computation, and experimental capabilities will enable tailor-made solvent systems that are suitable for a range of CO_2 sources and industrial applications, allowing much greater deployment of CCUS to meet international climate change commitments.

2.1.4 Conclusions

There is a significant opportunity to develop high-performance solvent systems using innovative chemistry. Fundamental understanding of chemical properties through newly developed tool sets will increase knowledge dissemination across the scientific community, allowing more accurate projections of performance at any scale for multiple capture sources. Significant advancement will reduce intermediate-scale testing requirements and accelerate the transfer of technologies into the marketplace.

Deployment of solvent capture requires fundamental knowledge of solvent loss mechanisms to facilitate mitigation. Increasing this knowledge demands the development of improved analytical methods to assess the mechanisms that provide input to tool sets to accurately predict behavior, qualify methods to reduce emissions, and reduce the degradation of solvents.

Process intensification (see the sidebar “Process Intensification”) optimizes available resources to maximize the use of solvent technologies. Whether through improved applications of materials, geometries, or process hybridization, intensification reduces size and enhances performance, leading to innovation.

The coupling of solvent chemistry improvement and loss mitigation with process intensification drives the advancement of carbon capture via the use of solvents, thereby lowering costs, reducing risks, and addressing environmental concerns. Solvent technology maturation time is expedited, leading to applications across the broad spectrum of CCUS opportunities.

2.1.5 Examples of Published Work

Demixing amine-based systems

Pinto, D.D.D., S.A.H. Zaidy, A. Hartono, and H. F. Svendsen. 2014. “Evaluation of a phase change solvent for CO_2 capture: Absorption and desorption tests,” *Int. J. Greenhouse Gas Control* **28**, 318–327.

Broutin, P., P. Briot, S. Ehlers, and A. Kather. 2017. “Benchmarking of the DMXTM CO_2 capture process,” *Energy Procedia* **114**, 2561–2572.

Zhang, J., Y. Qiao, W. Wang, R. Misch, K. Hussain, and D. W. Agar. 2013. “Development of an energy-efficient CO_2 capture process using thermomorphic biphasic solvents.” *Energy Procedia* **37**, 1254–1261.

Precipitation systems

Aronu, U. E., and X. Ma. 2017. “Liquid-solid solubility in AMP-KSAR-CO_2–H_2O system.” *Energy Procedia* **114**, 693–706.

Sanchez-Fernandez, E., K. Heffernan, L. van der Ham, M.J.G. Linders, E.L.V. Goetheer, and T.J.H. Vlugt. 2014. “Precipitating amino acid solvents for CO_2 capture. Opportunities to reduce costs in post combustion capture.” *Energy Procedia* **63**, 727–738.

2.2 Capture Panel Report: Sorbents and Looping Systems

Carbon dioxide capture processes based on the sorption/desorption of gases by solid materials have the potential to significantly reduce the energy penalty and equipment costs compared with state-of-the-art CO_2 capture technologies, such as amine scrubbing. These processes can principally be categorized into three groups based on different mechanisms: (1) physical adsorption/desorption of CO_2, (2) chemical absorption/desorption of CO_2, and (3) separation of O_2 by oxidation/reduction. These three categories use different types of materials and are operated at different conditions (i.e., temperature, pressure, gas atmosphere). A fundamental unifying theme, however, is that the solid material plays a crucial role in the energetic efficiency and cost of these processes, so the processes and materials must be developed hand-in-hand for any foreseen application. The following paragraphs provide a short overview of the basic principles of these processes.

The first category, adsorbent solids for carbon capture, can be classified generally by whether they chemically bond to CO_2 (stronger) or physically interact with CO_2 (relatively weaker). A stronger interaction with CO_2 typically offers the potential to enable higher selectivity and promotes a higher capacity of sorbed CO_2 at relatively low pressures—both desirable features. Conversely, the stronger interactions require more energy to regenerate a material, and so a proper balance must be found. This can be achieved by molecular-level design of capture materials (Figure 2.5). This ideal balance must consider the engineering process, as most sorbents are incorporated into temperature swing adsorption (TSA), pressure swing adsorption (PSA), or vacuum swing adsorption (VSA) systems. The approach relies on advanced materials with appropriate nanoscale features. There is no single "best" sorbent material; rather there will exist a perfect marriage of material and process engineering for a target separation. Advances in design based on the molecular building block approach, coupled with computer simulations and better means to probe materials in situ, have led to the ability to molecularly design new CO_2 capture materials. *Key challenges are to exploit such tailored materials and the synergies of integration in a predictive manner.*

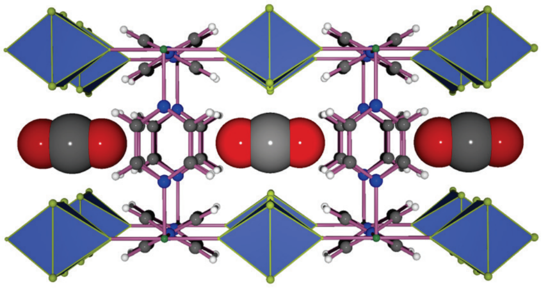
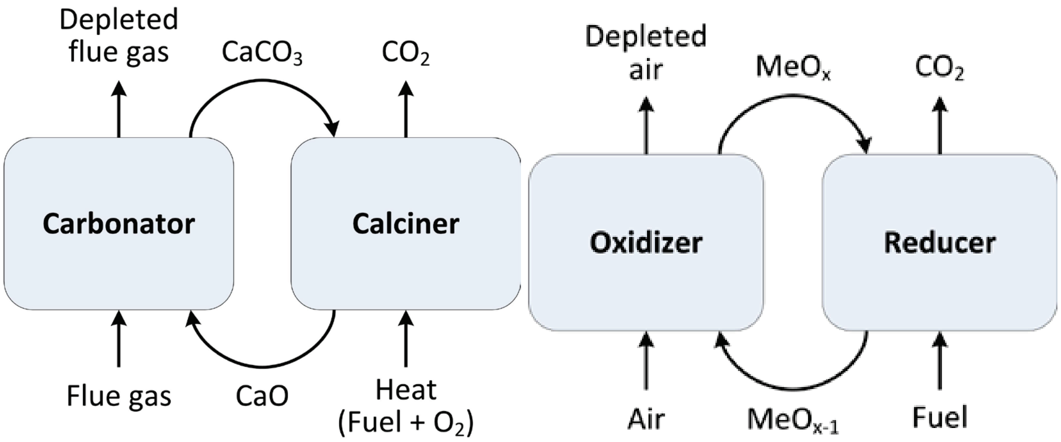


Figure 2.5. Experimental proof by x-ray diffraction of CO_2 molecules in designer nanopores in an advanced adsorbent, KAUST-7. | Reprinted with permission from Bhatt, P. M., et al. 2016. "A fine-tuned fluorinated MOF addresses the needs for trace CO_2 removal and air capture using physisorption." *J. Am. Chem. Soc.* **138**(29), 9301–9307. Copyright 2016 American Chemical Society.

The second category is based on the chemical absorption of CO_2 by a metal oxide to form a solid carbonate. The carbonate is then regenerated, releasing CO_2 at increased temperature. This cycling process is also called "carbonate looping." Calcium oxide (CaO) is the most promising base material, since limestone is abundant worldwide at very low cost. (In addition, potassium- and magnesium-based materials and hydrotolcites, zirconates, and silicates have displayed promising developments.) The CaO-based cycle is therefore also called "calcium looping." Calcium looping typically harnesses each reaction direction in a separate fluidized bed reactor, and the calcium compounds are cycled between the two. In the carbonator, CO_2 in a mixed gas stream combines with CaO exothermically, leaving a mostly carbon-free exhaust gas. The solid passes to the calciner, where it is heated to decompose endothermically to generate a pure CO_2 stream. Key to the efficiency of the technology is that the exothermic CO_2 capture step takes place at a temperature at which the liberated heat can be used in an efficient steam cycle to generate electricity and potentially repower existing plants. The calcium looping process is schematically shown in Figure 2.6a.



a) b)

Figure 2.6. The two looping systems: (a) the calcium looping system; (b) the chemical looping combustion system. | Image courtesy of Jochen Ströhle, Technische Universität Darmstadt

The third category, called "chemical looping," refers to the use of a metal oxide as an oxygen carrier intermediate to supply oxygen from air to a carbon-based fuel source, using a cycle redox reaction pathway (Figure 2.6b). Depending on the selected oxygen carrier material and reactor design, the redox chemical looping method can be configured for efficient gasification of carbon-based fuels to syngas—a building block for a wide variety of high-value chemical products—or can be designed for complete carbon-based fuel combustion for power generation applications, i.e., chemical looping combustion. The indirect combustion of the carbon-based fuel with oxygen supplied by the oxygen carrier intermediate from air eliminates the need for an air separation unit to perform oxy-combustion-based carbon capture. The result is a potentially highly efficient process scheme. The DOE milestone plan identifies chemical looping as the technology that has the highest cost-reduction benefit among all the methods, but it is also the one that is farthest from commercialization realization [Fan 2017].

2.2.1 Status of Sorbent and Looping System Technologies

Adsorbents

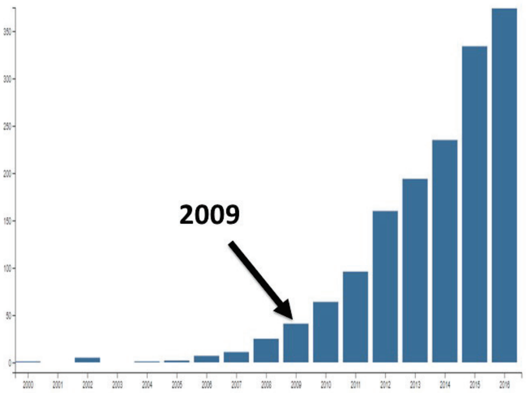


Figure 2.7. Chart of results of Web of Science search of "MOFs and carbon dioxide" spanning 2000–2016, showing >350 results for 2016. | Image courtesy of Mohammed Eddaoudi, KAUST

For adsorbent solids, in the 2009–2011 DOE-NETL study (*Evaluation of Solid Sorbents as a Retrofit Technology for CO_2 Capture from Coal-fired Power Plants* [NETL 2011]), a screening of prospective adsorbent materials was carried out that included 87 supported amines, 31 carbon-based materials, 6 zeolites, 7 supported carbonates, and 10 hydrotalcites. They break down into 104 chemisorptive materials and 37 physisorptive materials. The past 15 years has seen an explosion of new porous adsorbent materials (Figure 2.7) with features designable from molecular insights [Slater and Cooper 2015]. These include metal-organic frameworks (MOFs), covalent organic frameworks, and several other classes of porous polymer materials. A common feature of these materials is tunable micropores (< 2 nm pores) based on modular synthetic routes and the ability to probe structure at molecular levels [Yaghi et al. 2003]. *The prior DOE-NETL report did not include any of these classes of solids.* At the time, most of these materials—for reasons of chemical stability, performance, cost, or scalability—were not available/selected for study. Since then, these solids have spawned commercial ventures with multiple companies devoted to the manufacture of new classes of microporous solids. This progress has been spurred by the discoveries of molecular units that make robust materials while maintaining molecularly ordered predictable structures, and advances in simulating both the structures and performance of these materials. *Any preconceptions of these solids predating 2010 are not valid.* Some recent research outcomes that highlight the uniqueness of the materials and the potential for breakthroughs include MOFs with amine-appended micropores for capture in wet gas [Fracaroli et al. 2014]; MOFs with fluorinated pores that achieve selective CO_2 sorption through a combination of thermodynamic and kinetic means [Nugent et al. 2013]; MOFs that use a unique mechanism to bond CO_2 giving large capacity changes over small temperature ranges [McDonald 2015]; and solids capable of physisorbing CO_2 in the presence of water vapor [Bhatt et al. 2016; Shimizu et al. 2014].

To accelerate the physical adsorbent translation and deployment, it is imperative to bridge the gap between the adsorbent materials synthesis/characterization and the process system. It is necessary that the prospective adsorbent fulfill certain stability metrics before scale-up and further testing in a given process. Recently, a simplified but valuable experimental protocol was introduced to assess prospective physical adsorbents for carbon capture under flue gas stream conditions [Adil et al. 2017]. Realistically, the effective deployment of practical adsorption-based technologies depends on the development of made-to-order adsorbents expressing mutually two necessary requisites: (a) high selectivity/affinity for CO_2 and (b) excellent chemical stability in the presence of impurities in the flue gas, such as H_2O, SOx, and NOx. The implemented experimental protocol established the baseline performance of commercial adsorbents such as zeolite 13× and of activated carbon versus liquid amines, and introduced a standardized evaluation of the best reported MOFs for CO_2 capture from flue gas. This reference study shows the exceptional CO_2 capture ability of recently isolated MOFs with high chemical stability and a low energy for regeneration/recycling using different cycling modes. This finding affirms that MOF physical adsorbents offer the best compromise in satisfying all required metrics for efficient CO_2 scrubbing compared with the mature aqueous amines.

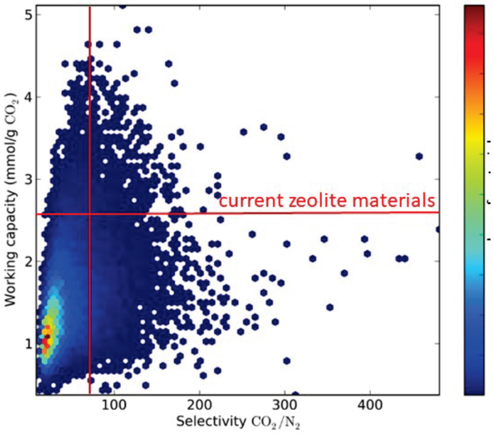


Figure 2.8. Prospects for better CO_2 capture materials in terms of selectivity and capacity based on simulations of new hypothetical structures. Red lines are present zeolite benchmarks. | Image courtesy of P. G. Boyd, PhD dissertation, University of Ottawa

Enormous strides have been made in the past decade in the field of atomistic computer modeling of porous sorbents. As result, modeling is an essential tool in the world's leading material discovery programs. If the molecular structure is known, simulations provide a precise picture of the interaction between the adsorbent and CO_2 at the molecular level and can accurately predict a material's adsorption properties. Whereas thousands of nanoporous materials have been synthesized and tested in the lab, databases of millions of plausible materials have very recently been generated in silico and screened for adsorption properties (Figure 2.8) to develop better structure–property relationships [Boyd 2015]. In some cases, the hypothetical high-performing material was subsequently synthesized in the lab and exhibited the predicted properties [Boyd et al. 2017]. Materials such as the SIFSIX family [Bhatt et al. 2016; Nugent et al. 2013] showed very high selectivity (close to infinity for CO_2 /N_2) and capacities close to MEA despite their lower surface area (<500 m^2/g). This class of materials unveiled a different mechanism for separation based on synergism between thermodynamic and kinetics of adsorption. Another material with relatively lower surface area is CALF20, which has unique CO_2 properties [Shimizu et al. 2014] offering high chemical stability and low cost for scalability. These developments show the importance of selectivity in contrast to high surface area. They attest to the need for discovery of new adsorbents offering in parallel the requisite chemical stability (wet conditions and tolerance of impurities), high selectivity, high capacity (8–15 wt %) and moderate heat of adsorption in the physisorption range of 35–54 kJ/mol.

The promise of a material must be assessed/modeled at a process level, as heat and mass transfer must be optimized; integration between molecular science and process engineering is needed. *This is a significant gap presently, and the promise of many new adsorbents is not realized beyond the lab bench*. There are many commercial adsorbent-based systems for CO_2 removal from a variety of gases (natural gas sweetening, CO_2 removal from air before cryogenic distillation). The goal of these systems is not to produce high-purity CO_2 for use or sequestration but to remove a nuisance gas, meaning CO_2 is removed at relatively low purity. However, there currently are few commercial adsorbent-based CO_2 capture systems at low temperature (<100°C). The development of processes for CO_2 capture at high purity is an active field. *There is currently no ability to quickly identify what processes and process conditions are optimal for a particular adsorbent to achieve the required specifications for a capture application*.

Carbonate/calcium looping

The most straightforward variant of calcium looping is based on using an oxy-fired calciner to provide heat for sorbent regeneration. The energy requirement for air separation is the main energy penalty of this process. The need for oxygen is around half that of a pure oxy-fuel–based power plant. Tests in several pilot-scale facilities on a MWth scale have proved the technical feasibility of this process variant, and it is ready for demonstration at semi-industrial scale [Abanades et al. 2015]. More recent research has focused on further process optimization. Significant reductions of the energy penalty can be expected when the consumption of oxygen can be greatly reduced or even completely avoided. Various concepts have been developed to increase the long-term cyclic capacity of the fuel and thus reduce the fuel and oxygen consumption in the calciner, such as sorbent regeneration by steam hydration, recarbonation, pre-treatment of limestone (e.g., doping with HBr), or synthesized sorbent materials. Novel rector concepts have been proposed, such as in situ combustion/carbonation and indirect calcination (e.g., through heat pipes). The latter avoids the need for oxygen and allows for using more sophisticated sorbents, since these are not in directly contact with a combustion environment. There has recently been significant interest in designing calcium looping plants that are flexible in power production. Alongside traditional turn-down and turn-up, medium-term (a few hours') storage of calcined sorbent is being studied. Calcium looping has synergies with industries beyond power generation. For example, in hydrogen manufacture from methane using sorbents, a larger, pure stream of H_2 is produced alongside a stream of CO_2. Spent CaO from calcium looping can be used as a raw material for cement production, eliminating a major waste stream while capturing CO_2 emissions from the plant. A similar reuse of sorbents can be achieved in primary steel manufacturing. Other innovative new applications continue to develop.

Chemical looping

The redox reactions appear to be simple in chemistry, but they are difficult to realize in practice because of various intertwining factors between the oxygen carrier materials and reactor design. Numerous lab-scale investigations have been performed to improve our understanding of the fundamental behavior and the synthesis techniques of metal oxide materials and their synergistic effects on reactor and system design, and hence to realize the desired level of CO_2 capture cost-effectively. Several large pilot plants, up to the MWth scale, have recently been operated to discern the feasibility of their commercialization for CO_2 capture [Ohlemüller et al. 2016]. One major challenge is to reach full conversion of the fuel in the reducer, particularly when solid fuels are used. Recently, much research has addressed the development of so-called CLOU (chemical looping with oxygen uncoupling) materials, since they have the capability to release molecular oxygen under reducing conditions, which strongly enhances the conversion of the fuel [Abanades et al. 2015]. However, currently available CLOU materials suffer from rather high production costs and only moderate material integrity. New reactor concepts, e.g., with internal or multiple stages, have been proposed for the reducer to improve fuel conversion.

2.2.2 Scientific Challenges

Four overarching challenges were identified for capture using sorbents, spanning both adsorbents and looping technologies:

1. Design and construct tailor-made materials with desired requisites for specific carbon capture applications.
2. Obtain better understanding of the structure–properties relationship at various levels: molecular (gas sorbent interactions), microscopic (thermal and mechanical properties, heat conduction management), and macroscopic (shaping, forming).
3. Enhance long-term reactivity, recyclability, and robust physical properties of materials within their working cycles.
4. Understand the relationship between material and process integration to produce optimal capture designs for flexible operation—bridging the gap between process engineering and materials science. This includes understanding and control of hydrodynamics, heat and mass transfer, and optimal process intensification.

Adsorbents

For adsorbents, there is a need to exploit the breakthrough materials developed in the past decade while pursuing the next generation. A knowledge base for adsorbents is ever growing from both the computational and the experimental perspectives. The adsorbent itself has many desirable features, and so even computationally assisted design requires numerous iterations to synthesize promising candidates, even on a bench scale. As Figure 2.8 shows, many exciting prospective materials have been predicted. In this context, it is important that there are many possibilities—not all materials may be synthesizable at sufficiently low costs. Another important opportunity for progress is that the current state of the art of modeling is based on knowledge of the atomic structure of the material and, in most practical applications, the materials are used in a structured form. A critical challenge is integrating the stated capture requirements in a single material in a complete process. The design of desired properties for an ideal carbon capture material begins at the nanoscale and must be informed by process requirements.

Beyond the nanoscale, there are microscale challenges to contacting the gas and adsorbent in a compact, efficient manner so that the driving force (e.g., cycling of temperature, pressure) can be applied with minimal use of energy and materials. Conventional adsorption processes relying on packed beds of beads or pellets (structured sorbents) have been used since the 1950s. When applied to CO_2 capture, these systems are not effective because of (1) extremely large volumes of gas, (2) the low pressure of process gas, and (3) low CO_2 concentrations. These issues lead to high pressure drops, limited mass transfer to and from the active sites of the sorbent, and poor heat management of the heat of adsorption/desorption. Research is needed to understand how best to synthesize and use tailored adsorbent structures and how to optimally expose the adsorbents to the gases in question.

A challenge is to match the material to the optimal process, specifically determining what driving force to use and in what combination (e.g., temperature, pressure, concentration) to adsorb and desorb, and to adapt this sequence of steps to the material and to the required specifications and feed conditions. This is a complex multi-variable, spatially distributed optimization problem and requires research to solve. There is a strong dependence of driving force on feed conditions—for example, PSA may be best for CO_2 capture from natural gas at high pressure, whereas VSA may be more appropriate for low-pressure applications. There is a strong synergy between the process and the materials used. Features unique to each adsorbent—such as CO_2 isotherm shape, heat of adsorption, selectivity, capacity, and mechanical and thermal stability—all influence the type and extent of driving force used to regenerate the adsorbent. Additional problems of impurity removal, heat management, and fluid flow must be solved; and novel integrated equipment must be designed (e.g., rotary valves, heat exchangers) to develop low-cost, energy-efficient, small-footprint solutions. Flexible operation of a capture plant is often needed—the ability to adapt the cycle (PSA, TSA, VSA) in real time to changes in demand or in feed rate is essential and needs research. Research opportunities lie in being able relate these needs to molecular structure and modeling. Doing so should lead to advanced materials that are designed with a clear understanding of how their different properties affect their performance in a real industrial process. These opportunities affirm the need for more multiscale modeling, synthesis, and testing in assessing new materials. Abanades et al. [2015] broadly screened 12 chemisorptive and 29 physisorptive solid sorbents, including eight MOFs. They stated

> Major improvements in the process performance of adsorption based systems can be achieved through combined developments of both materials and processes. The key strategy must be that of reducing cycle times, which can also lead to the use of more expensive novel adsorbents due to the reduction in the size of the units. A priority should be the development of structured packings or monoliths for novel families of adsorbent materials that are appearing in the literature on a regular basis.

Calcium/carbonate looping

Continued development of calcium looping in the mechanistic understanding of the complex high-temperature reactions taking place is required to increase the process performance. This applies in particular to how advanced materials stand up to repeated cycles of reaction in steam and other species, such as SO_2 and ash. The sorbents used in calcium looping are subject to thermal shock, high temperatures, contaminants, and particle collisions throughout the cycle. The reduction in reactivity due to high-temperature sintering in calcium looping systems is a major challenge. Maintaining higher levels of reactivity is critical for improving calcium looping performance in most applications. Calcium looping sorbents also attrit, falling apart and leaving the process as dust, a very significant issue for some sorbents. Solid sorbents also suffer from other degradation processes over time owing to a range of microscopic and macroscopic effects, such as sintering and contamination. Calcium looping advanced process design is essential to exploit new sorbents and to produce radical process improvements. One key advantage of calcium looping is the potential for integration with cement manufacturing, and how novel solid sorbents affect this synergy is an important field of research.

The sorbent must be replaced over time, increasing the operating cost and environmental impact of the capture process. Reducing these negative effects by enhancing long-term reactivity, recyclability, and robustness is a significant challenge for solid sorbents.

Chemical looping

Fundamentally, for oxygen carrier development, it is essential to understand the mechanism of oxygen release and regeneration in oxygen uncoupling and oxygen ion diffusion metal oxide materials, including at elevated pressure, and their effects on morphology variations of the materials. The chemical looping combustion process performance depends on oxygen carriers (particulate solids) that release oxygen and regenerate over thousands of cycles in high-temperature, mixed-gas environments. Furthermore, they are transported between reactors, causing physical impacts that do not often occur in non-looping systems. Thus, oxygen carriers must be morphologically stable over thousands of cycles while maintaining their oxygen capacity and mechanical stability despite particle collision, thermal shock, and gaseous impurities. However, good performance is also dependent on high-quality process design. Without the right conditions or process arrangements, the carriers can be rendered useless. Thus, the relationship between the process design and material design is paramount in developing a competitive chemical looping system.

The intrinsic long-term reactivity, recyclability, and robust physical properties of the oxygen carrier materials during the redox processes need to be ascertained. Understanding of the solid–gas reaction dictated by the intrinsic crystal lattice configuration is also needed to guide metal oxide design and engineering and robust oxygen carrier development for CO_2 capture applications, via a combination of both theory (thermodynamics of phase behavior, density functional theory analysis) and experiment. For instance, in Figure 2.9, scanning electron microscopy/energy-dispersive x-ray (SEM/EDX) mapping shows the addition of TiO_2 to an iron-based oxygen carrier can promote vacancies for ionic diffusion and provides a porous structure to enhance overall reactivity and recyclability. *It is important that the recyclability of the most promising materials be studied over 1,000 cycles by thermogravimetric analysis to discern the stability of the intrinsic reactivity and physical strength of materials before pilot-scale reactor tests.*

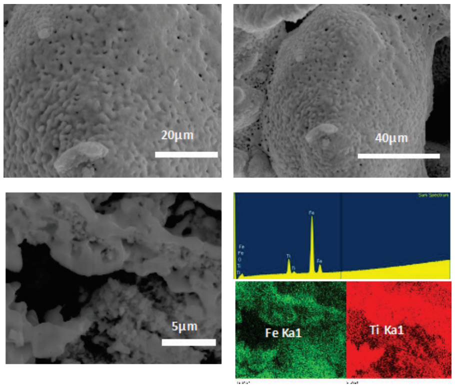


Figure 2.9. SEM/EDX mapping of a titanium support iron oxide particle after five redox cycles. | Republished with permission of Royal Society of Chemistry, from "Nanostructure formation mechanism and ion diffusion in iron–titanium composite materials with chemical looping redox reactions." Qin, L, Z., et al. *J. Mater. Chem. A* **3**, 2015 ; permission conveyed through Copyright Clearance Center Inc.

Looping systems in general

Understanding the relationship between the structure of a solid material and its properties is a major challenge in looping systems. Until now there has been insufficient work on building a systematic data set or chemical library that can be used to understand materials' interactions and properties; such a library is generally available for adsorbents and is very useful. This need for data applies across a range of scales: from the molecular level where the sorbent and gas interact; through the microscopic scale, where thermal and mechanical properties are observed; and up to the macroscopic effects of shaping and forming the sorbent particles. Without this knowledge, much research must rely on informed trial-and-error approaches that are resource-intensive.

The lack of an understanding of how the sorbent solids interact makes it difficult to design sorbents for specific applications. In tandem with this challenge, researchers must be able to apply the new understanding of sorbent behavior and properties to the manufacture of higher-performance materials. For example, if an industrial process works at a very high or low temperature, a blend of enhanced sorbent design and process optimization may provide a significant thermodynamic or kinetic advantage over a one-size-fits-all system design.

The performance of a sorbent is highly dependent upon the process configuration in which it is exploited; however, this is not particularly well understood, as it sits between process engineering and materials science. A challenge for solid sorbents is to better understand how to optimize the process design to allow valuable concepts such as flexible operation to become more common across the field. This example is particularly relevant for looping systems in which it is difficult to vary the flow rates through existing fluidized bed reactors; other options, such as thermal or chemical energy storage in the sorbent, are possible but have not been explored in sufficient detail. Models should make use of reliable experimental data to check assumptions and ensure they reflect reality. In particular, there is a need for more advanced and efficient computational fluid dynamics (CFD) methods for accurate prediction of the reactive two-phase flow in fluidized bed reactor systems, taking into account all relevant scales (including the mesoscale, i.e., clusters and bubbles) within such systems. There are also exciting opportunities in combining sorbent CO_2 capture with membranes for hydrogen separation in hydrogen manufacture; this will add another level of integration but could provide a step-change in hydrogen yield. Although the basics of how fluidized beds and other unit operations behave are well understood, some of the more complex, solid looping–specific challenges are still relatively unknown because of a lack of integrated process and material design. An example of a relevant up-and-coming research direction is pressurized operation of calcium looping and chemical looping reactors to improve efficiency. This will have knock-on effects for the sorbents used in the cycles; and optimization of the energy penalty, cost, and so on will depend on effective integration of process and material design. Novel reactor designs (e.g., moving packed beds) are also starting to be available in the field.

With regard to the applied aspects, large-scale production devices are needed to conduct cost-effective, efficient mass production of materials. Further, to study the reaction effects on the product yield, the multiphase contact mode and reactor must be selected considering the sorbent thermodynamic equilibrium and process transport phenomena. Sustained circulating fluidized bed operation using these materials needs to be ascertained before further reactor scale-up. The employment of nonmechanical devices for high level gas–solid flow control in a riser-fluidized system to minimize the CAPEX and OPEX of the looping processes is an essential part of the process system design. The overall volume of fluidized bed systems can be minimized by efficient looping operating schemes.

For adsorbent and looping technologies, both the fundamental and the applied work need to be conducted with the support of computation, modeling, and simulation efforts that are multiscale in nature, covering all scale ranges of molecules, particles, and processes.

2.2.3 Why Now?

Adsorbents offer enormous potential to significantly lower the cost of CO_2 capture from a variety of sources. The new classes of tailor-made sorbents that have emerged the past decade offer properties not attainable by conventional solids. They couple diversity with targeted molecular design. They can, based on lab-scale assessment and computational simulations, offer a step-change in the cost of carbon capture based on reduced energy requirements and smaller infrastructure needs. *The leading materials for* CO_2 *capture in these families have all been discovered/reported in the past 5 years*. CO_2 adsorption properties predicted by atomistic simulations have now achieved high accuracy and can be used as input for detailed process models of carbon capture systems (TSA and PSA) that have recently been developed. These will enable computational materials design that is fully integrated with process design. Furthermore, with the development of large databases of nanoporous materials that have been computationally screened, there are many opportunities to use big data machinery (e.g., machine learning) to help meet the challenges we have put forward. *Thus, game-changing adsorbents, better computational tools, and additive manufacturing methods are now available; and their use will lead to better* CO_2 *capture designs as well as opportunities to integrate conversion systems.*

There is a growing need to deploy capture technology in a wider variety of applications—e.g., iron and steel, cement, pulp and paper, ammonia production, and hydrogen synthesis. These are all ideal applications for adsorbent-based capture, as they frequently provide gases with high CO_2 partial pressure. However, there is no ability at the present time, with promising new materials in hand, to quickly identify what the best processes, process variables, and contacting devices are to achieve effective carbon capture for these applications, given a particular adsorbent.

For looping solid sorbent technologies, we are reaching the limits of current methods for material design and understanding. However, more powerful techniques such as in situ x-ray diffraction, transmission electron microscopy, x-ray photoelectron spectroscopy, nuclear magnetic resonance measurements, and multiscale modeling on high-performance computers have improved significantly in the past 4–5 years. These allow probing of materials as phases change during reactions. The tools are now available to design materials and processes in a more enlightened fashion and at a faster rate. Researchers will better understand the detrimental mechanisms that shorten the lifetimes of looping materials, and then investigate how to eliminate them. This capability will kick-start the development of breakthrough capture materials and processes that are highly competitive with other technologies in terms of cost, environmental impact, scale, and reliability.

In the past, the sheer number of complex processes occurring made detailed modeling extremely challenging, so existing models tend to be based on coarse approximations. Now, advanced molecular quantum and CFD simulations, which once required supercomputers, can be done on desktop workstations. This advance allows fast screening of novel reactor designs as new sorbent properties are measured, followed by their integration with detailed models at the process scale. Such simulations are particularly useful for solid looping systems, in which the use of fluidized, entrained, or moving beds may be envisaged—especially for plants running in flexible modes. Sorbent development processes that may previously have taken years now take weeks. Furthermore, the availability of several pilot plants allows validation of all of the above technologies at large scale, leading to a cycle of particle design, synthesis, CFD, and testing at scale.

The challenges facing energy storage in looping systems are particularly relevant now, as intermittent electricity generation's rapid roll-out and cost reductions dictate that carbon capture for electricity generation must be flexible enough to play a role in balancing the grid on the scale of a few hours. There is a compelling need to develop the most technologically viable and cost-effective methods for CO_2 capture now. Given recent important R&D progress toward both the fundamental and applied issues mentioned earlier, the commercialization of the chemical looping method for CO_2 capture can be realized and can follow the original DOE milestone timeline. For example, metal oxide particles have been made that sustain 3000 thermogravimetric analysis (TGA) cycles with no change in physical strength and little attrition in large-scale pilot plants. The proof of recyclability is a good indicator that the chemical looping method is viable. Clearly, more R&D effort will be needed on both fundamental and applied fronts to optimize both the materials and process performance so that this CO_2 capture method can be cost-effective.

2.2.4 Conclusions

The past decade has seen classes of new adsorbent porous solids (e.g., MOFs) emerge that can have their carbon capture properties designed at the molecular level. These solids have transcended the academic realm and have spawned commercial ventures based on their promise for practical applications [Trickett et al. 2017]. They will require significantly smaller infrastructure and lower capture costs. Recent broad screening studies of adsorbents have shifted to focus on physisorptive materials, whereas prior studies focused on chemisorptive amine-modified solids. Ongoing advances in experiment and modeling allow an optimal synergy of material and process that must be iteratively assessed on different scales of research. The materials are not limited to bed structures but are also applicable in membranes. They offer a step-change in capture/conversion through integration, rather than requiring decoupled processes. *These tailorable materials can be custom selected to maximize process efficiencies for a target gas separation.*

Calcium looping has made significant progress over the past few years, but to accelerate the rate of improvement, new methods and approaches are needed. *More systematic material development based on a comprehensive understanding of how calcium looping sorbents behave, alongside better multiscale process modeling, could lead to improved process configurations and to materials with better properties that can withstand the difficult conditions within the system, reducing cost and enhancing performance.* These breakthroughs will spur calcium looping and allow it to challenge more established capture technologies.

The redox chemical looping method developed as a technology for CO_2 capture is progressing well, based on the DOE timeline. For solid or gaseous fossil fuel processing, this technology—although it has been examined in the past—has garnered greater urgency now because of its important applications for CO_2 capture and other potential applications like hydrogen production. Additional research in basic science and applied engineering is critical in the maturation of the redox chemical looping method. Oxygen carriers that can sustain long-term reactivity and physical strength in a complex redox environment have been developed recently. This milestone signifies that, in time, this technology can reach commercial deployment.

2.3 Capture Panel Report: Membranes

Research and development during more than 50 years has led to a large variety of gas separation membranes. Since the first polymeric and inorganic membranes appeared, many new membrane materials, designs, and applications have emerged. The discussions in the membranes panel centered on the valuable contributions membranes can make to mitigation of CO_2 emissions in many industrial and power processes. Some important applications are natural gas sweetening; post-, pre- and oxy-combustion processes; CO_2 capture from industrial processes streams; and process intensification to improve yield and reduce energy consumption. Depending on the membrane type and operation conditions, flux and separation capabilities differ significantly. Thus, the optimal choice of membrane varies with the application. Continuously improving methods of synthesizing materials and manufacturing complex membrane designs with high permeance and selectivity have been a key factor in membrane development.

2.3.1 Status of Membrane Technologies

Polymeric membranes

Gas separation using polymeric membranes is a well-established field. Specifically, for hydrogen recovery, nitrogen production, natural gas treatment, and vapor recovery, polymeric membranes are used on a large scale. Membrane modularity and easy scale-up open opportunities for retrofitting existing plants, as well as flexibility with respect to the CO_2 capture rate. The technology has as well a near-instantaneous response, and a high turndown is possible that preserves plant operability. However, its application in large CO_2 capture processes in the power and industrial sector has not yet matured. Key challenges are related to the low partial pressure of CO_2 and the large scale required for flue gas treatment. For membranes to be cost-effective, further innovations in process design and membrane materials are thus needed.

Presently, commercial gas separation membranes are made from glassy or rubbery polymers, often largely amorphous, that operate based on the solution-diffusion mechanism [Wijmans et al. 1995]. Such membranes have broad free volume distributions and relatively nonspecific interactions between gas molecules and polymer segments. These limitations contribute to poor combinations of permeability and selectivity [Park et al. 2017; Koros and Zhang 2017] that fall well below the empirical Robeson perm-selectivity trade-off. Emerging materials for CO_2 capture membranes have been developed in recent years to improve permeability and selectivity. Such membranes—among other facilitated transport membranes (FTMs) that incorporate a “carrier component” in the structure itself—are attractive at the low CO_2 partial pressure experienced in post-combustion applications; and they show both high CO_2 permeance and selectivity for CO_2.

Polymeric membrane technology has been demonstrated at relatively large scale at the National Carbon Capture Center (NCCC) in the US state of Alabama at a 20 ton per day (tpd) scale. It employs the Membrane Technology and Research Inc. (MTR) membrane (Figure 2.10). A similar 6 tpd CO_2 capture demonstration has been executed at the NCCC using the Air Liquide cold membrane approach [Chaubey et al. 2017]. Moreover, the performance of FTMs has been evaluated at the Norcem cement factory in Norway employing hollow fiber membrane modules with 18 m^2 of membrane area [Hägg et al. 2017]. The test results indicated 70 mol % CO_2 purity can be easily achieved in a single stage. Polymeric membranes also present good stability—they have been exposed to high concentrations of SO_2 and NOx for a long period of time without significant performance change.

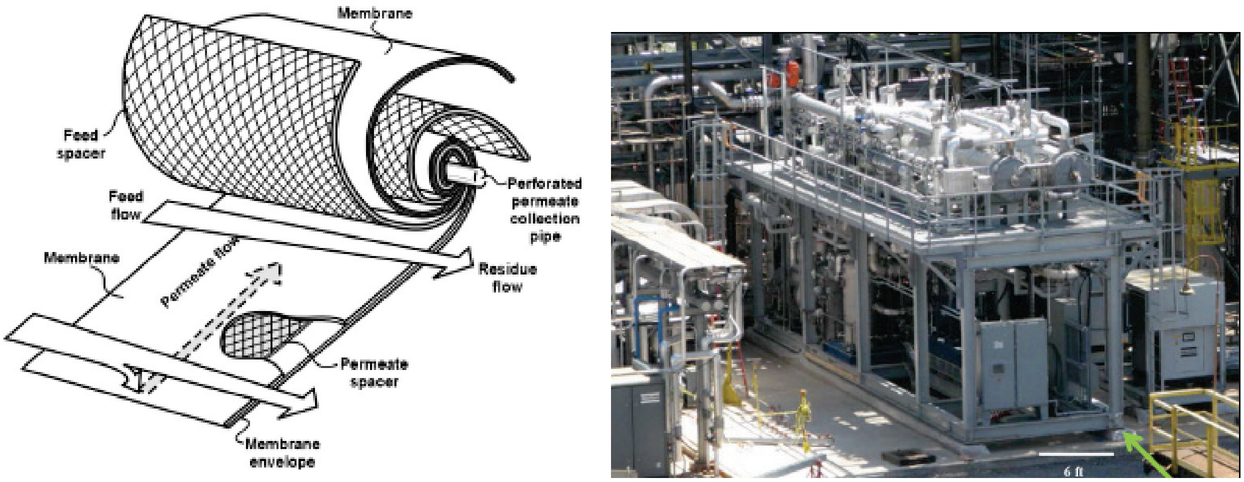


Figure 2.10. (a) Spiral-wound membrane module. (b) Installed 20 ton per day membrane demonstration facility at the National Carbon Capture Center in the United States, | (a) Image courtesy of National Energy Technology Laboratory; (b) Image courtesy of T. Merkel and B. Freeman, Membrane Technology and Research Inc.

Inorganic membrane systems

High-temperature gas separation membrane technology offers an opportunity to combine membrane separation processes directly with chemical reactions, leading to process intensification. Hence, it has the potential for significant cost reduction and higher efficiency of CCUS in power production and industrial processes. The most relevant separations are O_2 separation from air, and H_2 or CO_2 separation from syngas streams. A survey of integration possibilities for high-temperature membranes in power generation cycles with CO_2 capture is given in Bredesen et al. [2004]. In pre-combustion CO_2 capture schemes, ion-conducting oxygen transport membranes (OTMs) can be used for synthesis gas production either by partial oxidation of natural gas or by gasification of coal or biomass. They are also assessed for pure O_2 production. Air Products and Praxair have developed and demonstrated this membrane technology in units designed to produce up to 100 ton/day of O_2 and 1 MW of net power (Figure 2.11). Smaller-scale experiments have demonstrated high-purity O_2 production for over 15,000 hours.

Figure 2.11. (a) Intermediate-scale test unit, capable of producing up to 100 ton per day of oxygen; (b) installed ion-conducting oxygen separation modules. | Reprinted from *Solid State Ion.* 288, L. L. Anderson et al., Advances in ion transport membrane technology for oxygen and syngas production, 331–337, copyright 2016, with permission from Elsevier

Apart from small-scale application, pure O_2 production by the OTM route currently appears to be uncompetitive with cryogenic distillation. A more energy-efficient way to use OTMs is by full integration with the boiler, which is more challenging from a material perspective. The OTM syngas process—

combining air separation and high-temperature syngas generation processes into modular compact ceramic membrane reactors—has the potential to substantially reduce the capital investment for gas-to-liquid plants and for distributed hydrogen production (Figure 2.12).

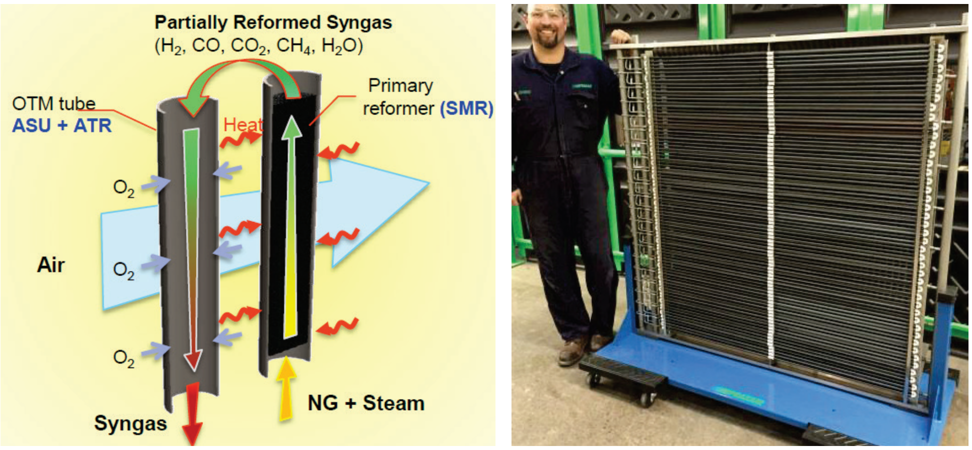


Figure 2.12. (Left) Principle of OTM syngas technology integrating steam methane reforming (SMR), auto thermal reforming (ATR), and air separation. (Right) Developed panel array of OTM and reformer tubes. | Image from Praxair 2016

The dense metal H_2-selective membrane technology for H_2 separation has progressed tremendously during the past 10 years. Such membranes allow production of CO_2-free hydrogen from syngas. Since Tokyo Gas demonstrated its membrane reformer (H_2 production capacity of 40 Nm^3/h, 150 kW_{th}) using natural gas as the feed, employing membranes with thicknesses of about 15–20 µm [Yasuda et al. 2003], efforts have mainly focused on the development and experimental verification of membranes employing much thinner palladium layers (i.e., <5 microns). A 98-tube membrane separator (1.8 m^2) has been tested in coal-derived syngas at the University of North Dakota Energy and Environmental Research Center [Schwartz et al. 2015]. Other activities include tests at the NCCC in Alabama [Castro-Dominguez et al. 2017] under adverse industrial conditions. Moreover, a 3 m^2 membrane module is currently being tested for H_2 separation on a syngas-side stream of the Statoil Methanol Plant at Tjeldbergodden, Norway, producing 25–100 Nm^3/h of H_2 [Peters et al. 2017].

Ceramic proton conductors are investigated for applications in membranes, fuel cells, electrolyzers, and sensors. In general, this membrane type is at an early development stage compared with the membranes described earlier. Efforts to establish membrane material compositions that combine high conductivities of protons and of electrons are needed. Research directions have been to combine metal or oxide electron conductors with proton-conducting oxides to obtain mixed-conducting membrane materials. Other directions have been to develop a single-phase mixed conductor (e.g., $BaCeO_3$-based) or to build a fuel cell structure (cathode–electrolyte–anode) to close the electric loop for the transport of protons and electrons (e.g., $BaZrO_3$-based electrolyte systems). More research is needed related to both the transport properties and the stability of the proton-conducting membrane concepts.

As alternatives to H_2 separation, high-temperature ceramic-carbonate dual-phase membranes can be applied to separate CO_2 from the other gas species at temperatures above 400°C. This early-stage technology gains from knowledge developed from research on molten carbonate fuel cells, and these membranes can allow for new process designs [Wei et al. 2015]. Dual-phase membranes may be applied in both post- and pre-combustion schemes [Anantharaman et al. 2016], but further work is needed to demonstrate their potential.

2.3.2 Scientific Challenges

The panel identified two research challenges of particular interest:

1. Transport phenomena in new membrane materials
2. Fabrication and use of the novel membrane systems in effective process design

Novel types of membrane materials have been developed in recent years. Next-generation materials such as thermal rearranged polymers (TRs); polymers of intrinsic microporosity (PIM); mixed matrix membranes (MMMs) employing MOFs, zeolites, or other nanoparticles; supported ionic liquid membranes; carbon molecular sieve (CMS) membranes; and FTMs have shown potential for enhanced performance related to selectivity and permeance. However, transport phenomena through these novel materials are less well understood. In particular, the behavior around interfaces (e.g., polymeric matrix/solid particles, polymeric dense selective layer/support layer) related to selectivity and diffusivity should be better understood (see the sidebar "Gas Transport in Membrane Materials"). The development of fundamental insights into the transport of small molecules through these barriers can lead to further improvements in these next-generation membrane materials. Moreover, these insights can lead to improvements related to the stability of membrane materials.

Inorganic membranes are mainly targeted for process integration at high temperatures; however, this increases the potential for reaction with gas components at the surface and for diffusion processes inside the material. This may lead to reduction of membrane lifetime.

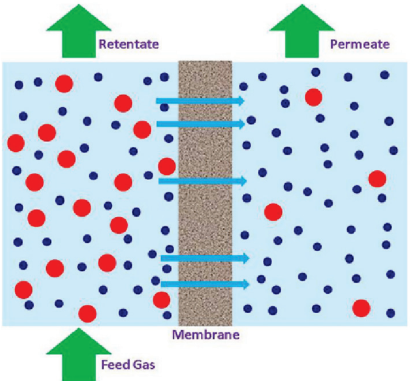
Recent investigations point particularly to the importance of reactivity and transport processes occurring at interfaces. To enable step-changes in membrane performance and stability, fundamental research is required to fill knowledge gaps about interfaces and how their properties can be controlled. The importance of interfaces can be exemplified for several cases:

- Dense mixed-conducting oxygen separation membranes deform during operation as a result of various stress fields. An important factor determining the extent and rate of deformation is the cation diffusion in grain boundaries [Anderson et al. 2016]. Furthermore, if a mixed-conducting oxide membrane contains more than a single cation that operates at high temperature in a large oxygen partial gradient, it may become kinetically unstable because of different cation diffusion rates. This may occur even if the material is thermodynamically stable in the surrounding gases [Fontaine et al. 2008].
- Proton-conducting $BaZrO_3$ membranes doped with yttria are known to have grain boundary resistance, which affects the permeability of protons. Charged defects in the grain boundary generate a space charge region extending into the grain, which influences the transport of charged species as protons. Space charge is not limited to internal grain boundaries but also may affect the properties of outer membrane surfaces and interface regions between membrane and electrode [Kjølseth et al. 2010].
- Recent studies of palladium-based membranes for hydrogen separation reveal voids concentrated along grain boundaries after long-term operation. Understanding how voids evolve could be important for defining membrane lifetime, as it is observed that pinhole formation slowly reduces selectivity [Peters et al. 2017].

In addition to understanding transport phenomena, the challenge is to use these novel membrane materials in effective membranes and membrane modules. The large-scale fabrication of a membrane consisting of a dense, thin layer of next-generation material on a support has many challenges. Currently, the fabrication methodology can be considered more as an empirical approach than as a thoroughly understood process that can be used for new materials. Membrane module design should be optimized for using these next-generation high-flux, thin membranes on optimized support structures. Methodologies for reducing the concentration polarization related to these high-flux membranes, and their applications, should be developed.

Gas Transport in Membrane Materials

The membrane permeability is the amount of a gas transported from the feed side to the permeate side through a unit thickness of the membrane per unit of (time × membrane area × partial pressure difference from feed to permeate side). Another commonly used unit, permeance, is the permeability divided by the membrane thickness. Permeance is a useful unit when the membrane thickness is difficult to define. Yet another common parameter is flux—the permeance multiplied by the pressure difference. Flux is often used when the driving force (partial pressure difference) is uncertain.



Schematic of gas separation membrane. | *Korean Journal of Chemical Engineering,* Carbon capture from stationary power generation sources: A review of the current status of the technologies, 30,2013, 1497–1526, M. Zaman and J. H. Lee. With permission of Springer

Gas separation in porous membranes requires pores of less than about 20 nm for Knudsen diffusion to take place. This mechanism results in low selectivity, determined by the mass ratio of the gas molecules. In microporous molecular sieve membranes with pores sizes of <1 nm, gas transport and selectivity are dependent on the surface–molecule interaction. Surface adsorption and diffusion properties are specific for different material–molecule combinations, and so the membrane separation properties will change with operating conditions. For instance, in a gas mixture of CO_2 and H_2, the membrane selectivity may change from CO_2-selective to H_2-selective with increasing temperature.

In dense polymeric membranes, the permeability is determined by the product of the solubility, S, and diffusivity, D, of the gas molecule (solution-diffusion mechanism). The permselectivity of two gases is given by the ratio of the permeabilities: $a = (S_aD_a)/(S_bD_b)$. As is the case for all dense polymeric membrane types, a transition of the molecule from the gas phase to the solid phase must occur. The permeability and selectivity expected from permeability ratios obtained in single-gas experiments may differ from observations obtained in gas mixtures. This effect relates to interactions of the gas mixture with the membrane, which may change the gas permeabilities to various degree. Dense hydrogen-selective metal membranes operate according to the solution-diffusion mechanism. In this case, hydrogen molecules are split at the feed side surface and transported in bulk as hydrogen atoms before recombining at the permeate-side surface to hydrogen molecules.

Dense ceramic membranes can separate hydrogen or oxygen by transport of protons and oxygen ions, respectively. These types of membranes are classified as either electrolyte (only ionic conduction occurs) or mixed conductor (both ionic and electronic conduction occur, and the permeation rate of the slower species will control the flux). For the electrolyte type, an external electrical circuit is required; therefore, these membranes require electrodes at both sides. The surface adsorption and reaction kinetics may limit the gas permeation rate for these dense inorganic membranes. Furthermore, for high-flux membranes, the gas phase diffusion to and from the surfaces may become limiting for the membrane permeance (an effect called concentration polarization).

Source: Zaman, M., and J. H. Lee. 2013. "Carbon capture from stationary power generation sources: A review of the current status of the technologies," *Korean Journal of Chemical Engineering* **30**, 1497–1526

2.3.3 Why Now?

In recent years, there has been steady improvement in polymeric membrane materials. Next-generation materials are being developed that have the potential for outstanding permeance–selectivity performance. The challenge now is how to use these materials in an optimized, effective membrane structure with stable performance.

The awareness of processes taking place in interface regions is increasing [Irvine et al. 2016]. It appears clear that some fundamental issues related to diffusion and segregation at interfaces can control transport and slow degradation processes that limit the performance of membranes. Flux-limiting processes and slow degradation processes require research efforts to close knowledge gaps, directed toward material synthesis, atomistic simulation, and advanced characterization that enable the investigation and control of matter at the nanoscale.

Real gases contain small amounts of various components, and membranes may be vulnerable to some of these. Since this is a membrane material–specific issue, it is most useful to attack this challenge specifically for each type of membrane. Therefore, research must address the stability of the emerging new membrane materials for CCUS. However, the challenge of developing efficient and sufficient pretreatments for gas mixtures fed to various CO_2 capture technologies is not specific for membrane technology.

2.3.4 Conclusions

Membrane separation has in a short time penetrated the market and become a preferred technology in a variety of applications. Its relevance in CCUS as an efficient, environmentally friendly, compact next-generation CO_2 mitigation technology is unquestionable. To obtain the potential benefits of membrane technology, fundamental research is needed to close knowledge gaps related to transport properties. This will enable the development of a new generation of membrane materials with improved performance and lifetime. Furthermore, research is needed to develop new design and fabrication methods to produce, at large scale, robust and highly permeable membrane structures. Finally, research is needed to develop new membrane materials to extend the current operation window and enable new process designs that reduce cost and energy consumption in CCUS applications.

2.4 Capture Panel Report: Combustion and Other Technologies

A broad range of combustion, partial combustion, and other capture-related technologies are considered to fall outside the areas of the solvents, membranes, and sorbents and looping systems.

The drive to identify novel combustion cycles that facilitate CO_2 capture is timely because it coincides with continual enabling advances in computing power and materials science that make new fundamental research enormously valuable for underpinning future deployment. High-intensity pressurized combustion research to date has been largely empirical and focused on short-burst firing of rocket engines, so the fundamental combustion science is not well characterized and cannot currently be accurately modeled.

Significant R&D and engineering successes elsewhere in the hydrogen value chain (transport and distribution, proton-exchange membrane fuel cells, storage and compression) make deployment of hydrogen as a low-carbon energy vector more probable than ever. Wide availability of hydrogen would be a significant decarbonization opportunity for industry, transport, heat, and electricity. Consequently, the latent demand for hydrogen is far larger than the amount that could be produced through electrolysis from constrained/curtailed renewables. However, relatively little research has been done on hydrogen production from fossil fuels with CCUS. These types of technologies will enable CCUS to play a much larger role in global decarbonization than electricity decarbonization alone and will capitalize on recent progress in hydrogen utilization technologies.

2.4.1 Status of Combustion and Other Technologies

The opportunities considered included those known by the expert panel as well as those presented in recent authoritative reviews [IEAGHG 2014; ZEP 2017] and are outlined below.

Combustion for CO_2 capture

Combustion-related and partial combustion–related capture must be applicable to a wide range of fuels ranging from conventional fossil-derived fuels (including less popular fuels such as heavy fuel oil), through an array of biomass fuels, to less conventional fuels such as ammonia and formic acid. The basic combustion problems are significantly amplified by limitations imposed by impurities in the products (e.g., NOx, sulfur oxides [SOx], unburned fuel, and heavy metals).

Decarbonized combustion technology is required at a wide range of scales, from utility-scale plants down to shipping scale and even further to road vehicles and domestic heating. At the utility or industrial scale, combustion science is generally employed to facilitate CO_2 separation, for example, through oxy-fired combustion or partial combustion. It is conceivable that these types of technologies could be reduced in size and modularized to enable, for example, oxy-fuel firing of heavy fuel oil on a ship with a consumed oxygen tank and a progressively filled liquefied CO_2 tank. Design for manufacturing techniques and mass production could enable significant cost reductions for this type of system if it were deployed in high numbers. However, at domestic and road vehicle scale, the weight, space, and CO_2 logistics challenges make the use of hydrogen produced centrally through partial combustion with carbon capture and storage (CCS) a more probable solution.

Additive manufacturing is already being deployed for key components associated with advanced combustion (Figure 2.13). It enables the use of much more intricate geometries than were previously possible. For example, microchannels in combined reactors/heat exchangers for steam methane reforming, ultra-compact heat exchangers, and even burner components have been 3D printed.

Figure 2.13. Siemens uses additive manufacturing to produce various turbine components. This burner head is made by Materials Solutions. | Image used by permission of Siemens. www.siemens.com/press

Cold thermophysical separations

A broad category of thermophysical separation techniques that can be used to isolate CO_2 from a flue gas stream, or to purify a stream of >60% CO_2 and raise its concentration to near purity, were noted by the panel as useful “other technologies” but were not proposed as PRDs.

Low-temperature CO_2 processing units (CPUs) are typically deployed downstream of atmospheric oxy-combustion plants, or in membrane separation systems, or on industrial CO_2 waste streams. Examples of systems built in recent years include the experience at Schwartzepumpe with Vattenfall and Air Liquide, and in Linde and Alstom systems. There is a reasonable quantity of published research, including a textbook [Zheng 2011], the ZEP [2017] future CCS technologies report, and an account of the CPU operated on a small oxy-fuel boiler at Callide, Australia [Lesort 2015].

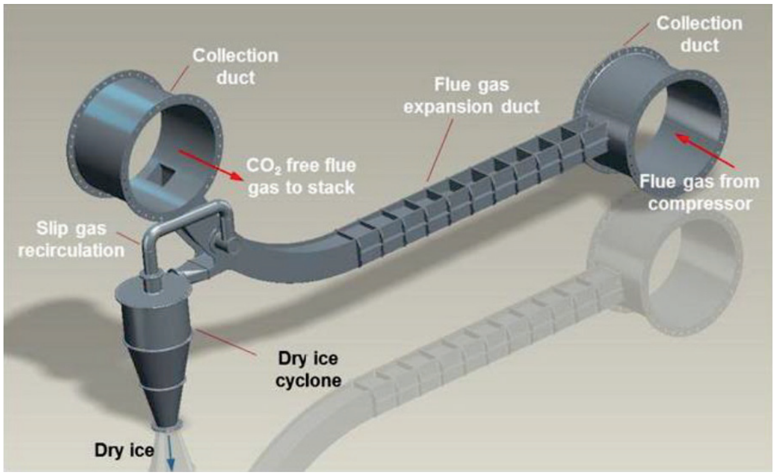
It is possible to remove CO_2 from flue gas through desublimation, for example, using supersonic separation (see the sidebar “Supersonic Separation”). A number of groups have worked on this effort, including Sustainable Energy Solutions [Baxter 2016] and ENGO Engineering [Imaev 2014]. The latter has a particular interest in enabling the exploration of natural gas fields with CO_2 content that is currently too high for economic development. Work has been done at the Paris School of Mines [Freeman 2007] to evaluate potential process configurations and economics.

Combustion alternatives

A number of alternatives exist for extracting chemical energy from fuel without traditional combustion. One interesting area is the molten carbonate fuel cell (MCFC), a high-temperature, high-efficiency form of fuel cell that uses CO_2 to form a carbonate electrolyte that can be fueled with non-hydrogen fuels. It has been demonstrated that these fuel cells can be used to strip CO_2 from a relatively impure stream of methane or from flue gas. MCFC power plants have been built that produce up to 59 MWe using 21 fuel cells [McPhail 2015]. For large-scale operations, such as CO_2 capture from power utilities or heavy industry, large numbers of these fuel cells are intended to operate in parallel. It is likely that innovative arrangements and housings will have to be developed to enable this approach, given the high operating temperature of the fuel cells and the extensive flue gas ductwork that would be required. Direct carbon fuel cells are also available [Munnings 2014].

Supersonic Separation

The principle of supersonic separation is that flue gas is directed to a converging diverging nozzle and expanded to supersonic velocities. Aerodynamic expansion to high velocity results in the conversion of potential energy contained in the form of pressure and temperature into kinetic energy, resulting in a rapid temperature and pressure decrease and the condensation of undesirable constituents of flue gas including the desublimation of CO_2. The high density of the solid phase constituents of the flow allows for inertial separation by centrifugal forces induced by flow path curvature. The image below shows the configuration of an individual inertial CO_2 extraction system. | Image created by National Energy Technology Laboratory (*Assessment of Emerging CO_2 Capture Technologies and Their Potential to Reduce Costs,* IEAGHG 2014, Figure 25)



Catalytic combustion, an alternative to traditional combustion, has been the subject of significant research since the 1970s, including work by Precision Combustion Inc. [Etemad 2011] and others. Catalytic combustion has been used extensively in the industrial production of CO_2

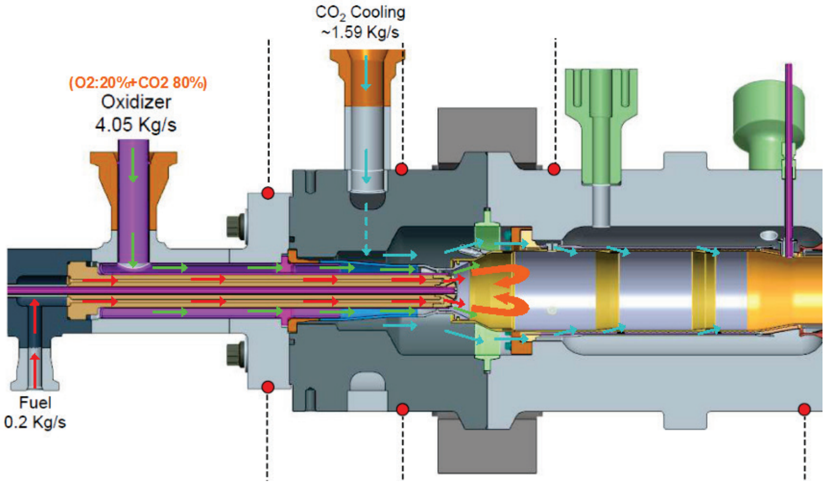
[Zheng 2011]. More recently, it has been considered for final polishing of CO_2 in CCS for oxy-combustion technologies and for chemical looping combustion where oxygen and unburnt fuel concentrations are reduced, respectively. The catalysts used are similar to those used in catalytic converters of automobiles, in which catalytic combustion also proceeds.

High-intensity combustion

A number of high-intensity combustion cycles are now under investigation. They include the Allam Cycle (see the sidebar "Pressurized Oxy-Combustion"), which uses recycled CO_2 as a key constituent of the working fluid; cycles that use argon as an inert working fluid; direct-contact steam generation that produces steam without boiler tubes; and a variety of cycles intended for use with solid fuels.

Pressurized Oxy-Combustion for High-Pressure Cycles

Pressurized oxy-combustors use purified oxygen combined with a temperature moderator to burn fuels at high pressure. In place of the nitrogen found in air, CO_2 and/or steam are to be used as the temperature moderator and also subsequently as a working fluid that is expanded through a turbine to generate power. The combustor pictured here is a high-pressure (300 bar) oxy-combustor for use with gaseous fuels using CO_2 as the temperature moderator. It is a key component in a power cycle using CO_2 as a working fluid that is predicted to generate power from natural gas with 100% CO_2 capture at 58% to 59% efficiency (lower heating value basis). | Image courtesy of Rodney Allam, NET Power

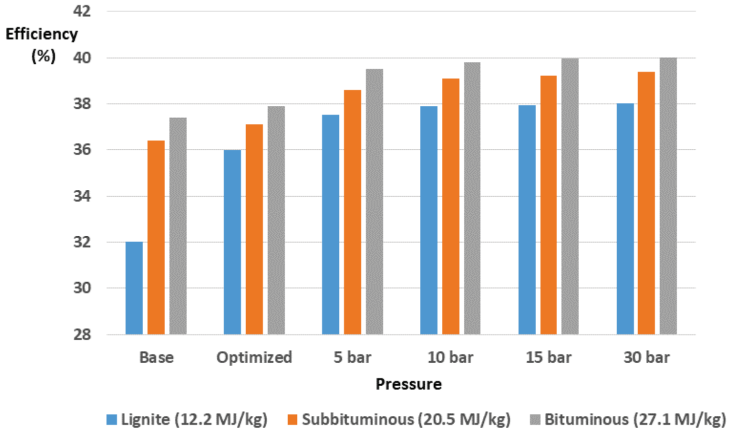


A key enabler of these types of cycles is the use of high-pressure combustion. Combustion for heat generation has mostly been conducted at near-atmospheric pressure for millennia. However, pressurizing combustion offers a number of advantages (see the sidebar "Efficiency Benefit of Pressurization"). Vehicle internal combustion engines have been using superchargers and turbochargers for many decades to improve performance. These engines fall in the range of tens of kW to tens of MW and are suitable for thousands of hours of use. Rocket engines also use high-pressure combustion and can be much higher capacity—gigawatt scale—but typically only run for minutes and have often been developed by trial-and-error.

A number of industry participants are becoming interested in high-pressure combustion technologies, including methane–oxygen rocket engines [Newton 2015]. Clean Energy Systems has done work with steam as a recycling fluid at up to 200 bar at the 200 MW scale [Prenske 2013] and NetPower with CO_2 as the recycling fluid at up to 300 bar [Allam et al. 2017]. However, most work has been done on example test units at a limited range of operating points, and not on units integrated into complete systems.

Efficiency Benefit of Pressurization for Different Fuels

In the same way that the boiling point of water changes with changes in atmospheric pressure, the boiling point of water in flue gas changes with pressure. If we condense the water in flue gas at high pressure then we are able to use the heat generated at higher temperature thereby increasing the efficiency of the system. The chart below shows how much efficiency increases for a power generation cycle for coals with differing moisture contents from atmospheric pressure ('Base' and 'Optimized') up to 30 bar pressure. The benefit of pressurization is greatest for the fuel that results in the most water present in the flue gas; lignite shown with blue bars. The benefits to biomass will be substantial due to its high moisture and hydrogen content. | image courtesy of Jon Gibbins, University of Sheffield, UK. Data from Tumsa, T., T. Mun, U. Lee, and W. Yang. 2017. "Effects of coal characteristics to performance of a highly efficient thermal power generation system based on pressurized oxy-fuel combustion," *Int. J. Energy Res.* **41,** 127-138



Many high-pressure combustion processes—particularly those that work at pressures above a few tens of atmospheres—choose to use oxygen rather than air as a reagent to avoid the energy cost of compressing the nitrogen present in the air. Currently, high quantities of oxygen are obtained using a cryogenic air separation unit, which is a well-established but relatively expensive technology (see the sidebar "Direct-Contact Steam Generation").

Despite this activity, there is no good review article on high-pressure utility-scale oxy-combustion. Most of the existing literature is focused on rocket engines, gas turbines, and magnetohydrodynamic generator combustors.

Direct Contact Steam Generation

In this high-pressure combustion technology, process waste water comes into contact with the products of an oxygen-fuel flame to generate a mixture rich in steam that can be used in industrial applications. Costs are greatly reduced for zero emission steam generation since water treatment facilities can be nearly eliminated and no boiler is required. The CO_2 is captured when the steam condenses in the industrial application. Applications for this type of steam generation could also include power plants. Here very high temperature supercritical steam can be produced with less severe limitations from metallurgy compared with conventional boilers. Because of the direct contact of the combustion products with the water, the system is also highly efficient, requiring about 10% less natural gas than conventional steam generation processes; but a downside is the more corrosive mixture of CO_2 and water in a condenser. Pictured here is a research scale 100 bar oxy-direct contact steam generator including combustor, scrubber and steam filters at CanmetENERGY in Ottawa, Canada.

A description of the technology integrated with heavy oil production is available at https://youtu.be/juRNCwus5YU

Image courtesy of CanmetENERGY–Ottawa

Hydrogen

Hydrogen offers significant opportunities for decarbonization beyond electricity generation—it has additional applications in a wide range of heating fuels, transport fuels, and industrial feedstocks. However even at today's relatively modest hydrogen production rates, electrolysis is a niche means of hydrogen production; 96% of hydrogen is derived from fossil fuels (Figure 2.14). Production of zero-carbon hydrogen from fossil fuels show signs of becoming very important for carbon capture and thus should remain a priority focus area.

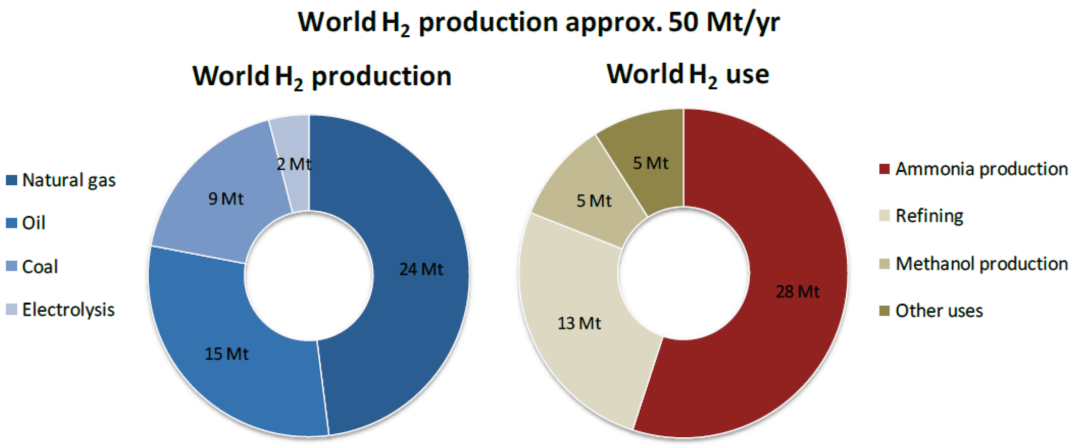


Figure 2.14. Estimated world hydrogen production and use in 2008. | Reproduced with permission from Zakkour and Cook. 2010. *CCS Roadmap for Industry: High Purity CO_2 Sources.* Carbon Counts Company.

Hydrogen (H_2) production through partial combustion (or partial oxidation/gasification) is a process that has much in common with full combustion [Volsund et al. 2016]. In the CO_2 capture context, the process could be used to generate a synthesis gas (syngas) that is then shifted to form H_2 and CO_2. Partial combustion/pyrolysis also creates the opportunity to intercept the carbon as solid elemental black carbon. Resource utilization efficiency disadvantages aside, in some circumstances (for example, for small/remote emitters or mobile units), collection of black carbon may be preferable to CO_2 collection simply because of the ease of handling it at atmospheric pressure; the form of the solid carbon produced is likely to be an important factor.

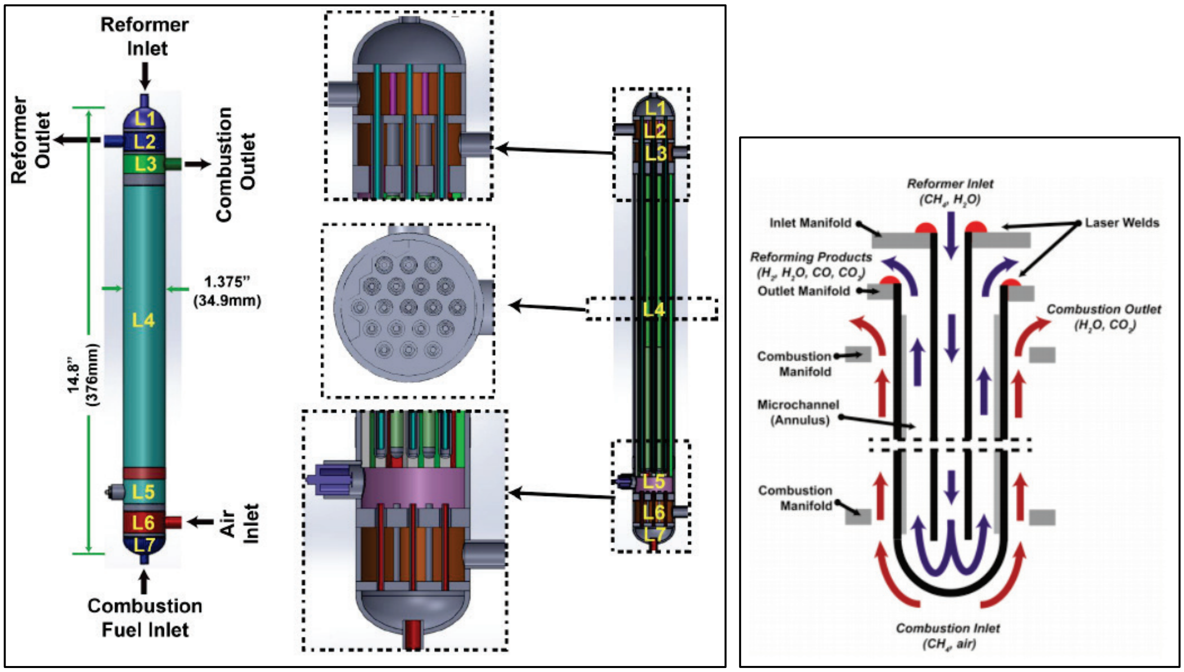
Gasification development is considered to require predominantly higher-TRL activities, as also would any further development of large-scale syngas production by conventional catalytic or noncatalytic reformers or improvements in oxygen supply from cryogenic air separation technology. *Reforming with oxygen supplied via high-temperature membranes and integrated with hydrogen production was proposed by the panel as an area in which lower-TRL fundamental research is critical to achieve breakthroughs. Linking combustion and reforming, e.g., in microchannel reactors, also offers significant scope for cost and performance improvements, particularly for distributed hydrogen production.*

Microchannel reactors (see the sidebar “Integrated Combustion/Microchannel Reforming”) allow close matching between heat supply and demand for hydrogen production through reforming. The matching includes the scope for counter-flow operation, thus increasing the efficiency of operation, particularly at smaller scales. Microchannel reactors are good examples of process intensification, i.e., making processes more compact and efficient. Systems containing microchannels lend themselves to novel integrated processes for hydrogen production, such as the direct integration of hydrogen-permeable membranes with microchannels for integrated CO_2 capture. Separate processes for oxygen production (to replace air as the oxidant) and CO_2/H_2 separation, e.g., using membranes, can also be combined with the style of microchannel reactor shown in the sidebar.

In addition, the combustion of hydrogen itself offers novel fundamental challenges—both for pressurized, high-intensity combustion in gas turbines and in applications such as hydrogen-fired reformers and other industrial/domestic applications in which satisfactory heat transfer must be achieved from the unconventional flames that hydrogen produces.

Further research and engineering innovations are obviously needed throughout the H_2 supply chain and consumption infrastructure. However, this report does not cover them in detail as they are beyond the scope of combustion and/or require higher-TRL development activities.

Integrated Combustion / Microchannel Reforming



All images from H. Butcher 2017. *Integrated Steam Reforming/Catalytic Combustion Annular Microchannel Reactor For Hydrogen Production*. PhD dissertation, Texas A&M University.

Combining high-intensity combustion, compact heat exchange technology, and microchannel reactors will permit scalable, affordable and efficient hydrogen production [Haynes 2011].

The concept can be described simply as an array of autothermal methane reforming (AMR) tubes that transport, heat, and catalyze reformer gas. Between the tubes, there is open space in which combustion gases flow, providing heat for the reforming process [Butcher 2017].

Natural gas (CH_4) and steam (H_2O) are fed into the reformer inlet L1 and reformed in the L4 chamber containing the AMR array of tubes. At the same time, CH_4 and air (or oxygen with temperature moderator) are fed into the air and combustion fuel inlets (L6 and L7) and combusted in the catalytic combustion chamber (L5). Reforming products H_2, CO, CO_2 and H_2O leave the reforming outlet L2, and combustion products H_2O and CO_2 leave the combustion outlet L3 [Butcher 2017].

The AMR tubes are based on micro-technology, which promises an inherently safer, more portable, and efficient alternative to industrial-scale reactors. The reduced hydraulic diameter associated with reaction volume may lead to order-of-magnitude improvements in heat and mass transfer rates. This allows for higher chemical productivity per unit of volume at greater power densities, in turn realizing a more compact and portable reactor [Butcher 2017] .

2.4.2 Scientific Challenges

There are two major areas in which advances are critically needed: (1) new approaches for high-intensity pressurized combustion and (2) alternative lower-cost technologies for hydrogen production from fossil fuels with CO_2 capture through effective combinations of reforming and combustion

The fundamental research challenges identified for high-intensity pressurized combustion include the following:

- Better models validated against experimental data, including reaction kinetics; three-body collision reaction mechanisms; speciation; hydrodynamics; flame speed and burner stability; heat transfer and heat profiles; impurities; devolatilization (for solid and liquid combustion); and transport properties
- High-pressure flue gas cleanup techniques for SO_x/NO_x/O_2/particulates
- New measurement techniques within the combustion space
- High-pressure corrosion, slagging, agglomeration, and fouling mechanisms, including mitigation methods and materials
- Impact of impurities
- Balance of plant
- Composition of water and other waste streams
- Fuels—conventional (coal and natural gas) and less conventional (e.g., biomass, heavy fuel oil, ammonia)
- Direct oxygen supply via ion transfer membranes incorporated into combustors—a key low-TRL research activity that overlaps syngas production through partial oxidation

The following are research challenges identified for lower-cost combustion-based technologies for hydrogen production with CO_2 capture (see conventional hydrogen production with CO_2 capture in the sidebar "Hydrogen Generation from Fossil Fuels"):

- Use of catalytic microchannel reactors in novel process reactor designs (including improved cooling systems and high temperature materials for H_2 fired reformers)
- Oxygen supply for partial-oxidation reforming via chemical looping reforming or membranes
- Novel H_2 purification technologies including cryogenic and membranes
- Improved system design for effective heat recovery (e.g., using convective reforming) to increase H_2 production/yield and reduce unwanted steam production
- Heat and energy flow integration with power systems

2.4.3 Why Now?

In both of the identified areas, high-intensity pressurized combustion and alternative lower-cost technologies for hydrogen production from fossil fuels with CO_2 capture through effective combinations of reforming and combustion, many recent advances in relevant areas can propel research to address today's limitation.

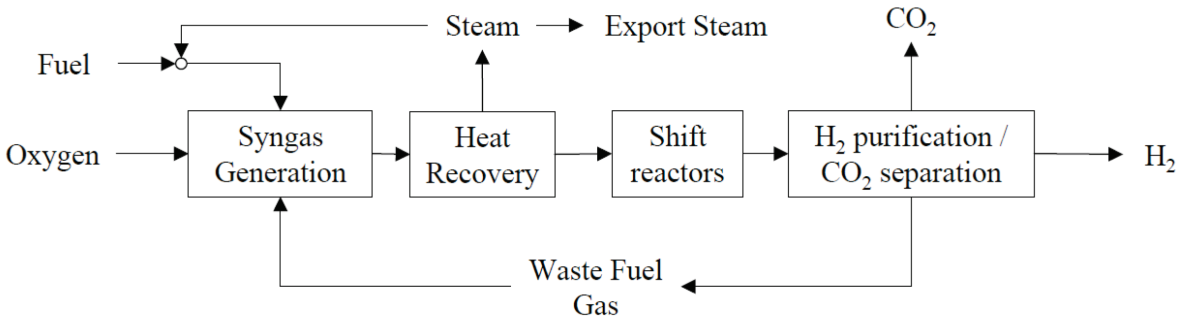
High-intensity pressurized combustion is a relatively new field that has been largely focused on limited aerospace and military applications. However, the need for carbon capture has sparked interest in and development of novel thermodynamic cycles that require pressurized combustion. For example, a number of first-generation oxy-fuel plant and concept studies have shown that high-pressure combustion cycles have high efficiency and the potential to be inexpensive.

Another advance is that more powerful supercomputers are approaching the speed necessary to perform the myriad of complex calculations required to simulate the three-body reaction kinetics and hydrodynamics in a high-pressure combustion reaction. The results could be helpful for design optimization through simulation rather than by empirical experimentation.

As high-pressure combustion typically leverages very high temperatures to seek efficiency gains, it ideally requires materials that can withstand higher temperatures and pressures to simplify heat exchanger design. Recent progress in high-temperature, high-pressure alloys will enable the design of equipment with creep lifetimes that were impossible a decade ago. This will be an important contribution to the robustness and longevity of systems related to high-pressure combustion.

Hydrogen Generation from Fossil Fuels with CO_2 capture

Conventional steam/natural gas catalytic reforming is not ideally suited to zero-carbon hydrogen production. CO_2 capture is easier via methods in which a synthesis gas (syngas) comprising mixtures of H_2 and CO is converted to pure hydrogen using known steps of CO reaction with steam to produce H_2 and CO_2, followed by purification and separation of H_2 at high recovery using conventional methods such as chemical/physical solvent, pressure swing multi-level absorber or low temperature membrane. | Image from Allam 2004



A number of areas of research are required to facilitate the production of low-cost H_2 with zero CO_2 emissions, mostly focused around simplifying and combining the stages above:

- The integration of H_2 and power production for better use of heat
- Systems such as catalytic microchannel reactors to integrate combustion and reforming and achieve improved performance and more compact reactors
- Oxygen ion transport membranes to supply the oxygen required for partial oxidation to produce a syngas stream and novel hydrogen separation methods, for example, using cryogenics or membranes

Finally, ion transport membranes are emerging as enablers of both hydrogen production and high-pressure combustion. New improved molecular modeling techniques for solid lattice structures—in particular, long-range interactions through lattice structures—offer great potential to improve the performance and cost of these membranes.

Alternative lower-cost technologies for hydrogen production from fossil fuels with CO_2 capture through effective combinations of reforming and combustion have particular potential due to recent advances. A number of macro-economic factors have created significant demand for widely available low-carbon hydrogen. For example, energy-exporting nations like Norway export ~20 TWh of electricity but have the potential to export 700 TWh of H_2 [Røkke 2017]. Announcements from vehicle manufacturers and European governments suggest there will be a steady shift away from diesel and gasoline, with hydrogen (or hydrogen fuel cell) powered vehicles offering a strong alternative to electric vehicles in high-utilization applications. The UK Committee on Climate Change has stressed the need for large-scale hydrogen production, with CCS as a critical element of deep decarbonization of heat for buildings. No other low-carbon options can match the characteristics of current natural gas supplies. Global hydrocarbon production companies are now expressing interest in hydrogen as they migrate toward becoming “energy providers” rather than oil and gas companies.

Significant know-how in hydrogen technologies has been built up to solve many of the high-pressure storage, refueling, pipeline transport, and consumption challenges for hydrogen as an energy vector. There is real potential to convert whole cities from natural gas to hydrogen using the existing infrastructure with limited retrofit changes [Northern Gas Networks 2016]. Hydrogen development may now be limited only by the availability of large-scale supplies of zero-carbon hydrogen.

Just a few decades ago, it was considered to be too expensive to transport natural gas any distance, so there was widespread flaring and venting. Now, natural gas is routinely traded globally, and there is a rapidly shrinking arbitrage margin between the Henry Hub price and similar hubs in Asia or Europe [BP 2015]. Hydrogen has the same potential if it can be manufactured in appropriate volumes.

2.4.4 Conclusions

The panel concluded that the two areas in which fundamental R&D would lead to major breakthroughs in broadly applicable carbon capture technologies are (1) high-intensity pressurized combustion and (2) alternative lower-cost combustion-based technologies for hydrogen production from fossil fuels.

Pressurized combustion has been a relatively neglected area of fundamental research limited largely to short-burst firing of rocket engines. The drive to maintain or improve efficiency while producing CO_2 in an easily captured and compressed form has made it imperative to overcome the challenges of extending operating times from minutes to years. Simultaneously, advances in computing power and materials are making possible fundamental research to support these challenging objectives.

The wide availability of zero-emission hydrogen is a significant opportunity for decarbonization of many sectors of the economy, including industry, transport and heat and power production. Work on this carbon-free vector is imperative to leverage the benefits of CCS beyond electricity production and industrial applications. The quantity of hydrogen required is larger than can be produced through electrolysis from constrained/curtailed renewable energy sources. Hydrogen has potential for deeper decarbonization than electricity (e.g., in heat and transport), but providing the necessary large volumes of zero-carbon hydrogen will not be possible without production from fossil fuel with CCS. Current hydrogen production technologies are not optimized for CO_2 capture.

2.5 Carbon Dioxide Capture Priority Research Directions

2.5.1 PRD C-1: Designing High-Performing Solvents for CO_2 Capture

The primary technological challenge associated with CO_2 capture systems is cost, both operating (OPEX) and capital expenses (CAPEX). The greatest opportunities for further cost reduction for the most advanced and least expensive technology (i.e., advanced aqueous amine systems) are in capital expenses. Since aqueous amine systems have been expertly engineered over the past several decades, an important route toward significant cost reduction is in completely new molecularly designed solvents and processes. By marshaling state-of-the-art molecular modeling and simulation tools, in combination with advanced synthesis and design capabilities, we now have the opportunity to design new solvents and mixtures explicitly tailored for efficient, lower-cost capture of CO_2 from various sources.

Scientific Challenges

Figure 2.15 conceptualizes the desired approach for developing advanced solvents for CO_2 capture. To design high-performance solvent formulations and integrate them into optimized and intensified processes, several research challenges must be tackled. One consists of developing a synergistic understanding of solvent attributes and process features. Elucidating structure–properties relationships (physical and chemical, thermodynamics and kinetics) is the critical knowledge to acquire in order to rationally design and optimize solvent systems directed to specific CO_2 sources. Process design should accompany the study of high-performance solvents with mastered properties to lead to synergistic development of an optimized and tailored solvent-based process.

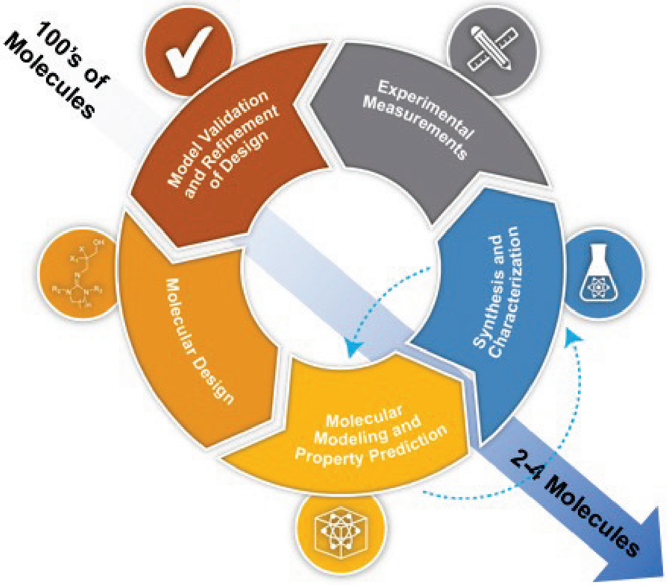


Figure 2.15. Conceptual integrated solvent development pipeline. | Image courtesy of Pacific Northwest National Laboratory

The exact properties of an ideal solvent may vary from one CO_2 source to the next (e.g., post-combustion capture from pulverized coal plants vs. natural gas–fired plants vs. cement manufacturing and other industrial emission sources). Process conditions may also depend on the downstream use of the separated CO_2 stream. With the knowledge gained from research, combined capture and utilization can ultimately be addressed. From this perspective, solvent development needs to be integrated with process development. The challenge is to design new solvent systems with the necessary combination of physical and chemical properties that will result in high-performance CO_2 capture systems.

The enthalpy of absorption and/or reaction is critical to determining energy demand and subsequent operating costs. It is recognized that second-generation aqueous amine processes remarkably require only about twice the thermodynamic minimum energy [Zhang et al. 2016], so further reductions in energy requirements may face diminishing returns. Conversely, advanced solvents are starting at this level of efficiency and are expected to be optimized further with continued study. The entropy of absorption/reaction plays a role in determining capacity, but this property has been largely ignored in the selection of CO_2 capture solvents [Septavaux et al. 2017]. Greater understanding of it may lead to new process configurations. Fast CO_2 absorption and desorption, as determined by reaction kinetics and/or mass transfer, must also be integrated in the solvent design because they greatly affect capital costs. The solvent must also show minimal corrosivity with inexpensive materials of construction and have an acceptably low environmental impact, as determined by such properties as vapor pressure and toxicity.

The scientific grand challenge is to design new solvent materials for these multiple chemical and physical property requirements, simply from knowledge of molecular structure.

Research Directions

To reach the goal of understanding solvent attributes requires the design of new tool sets for the development and prediction of solvent properties. They will enable benchmarking of the performances of the new systems through not only molecular but also multiscale process modeling and simulation. The development and use of this tool set will require multidisciplinary work teams (theoreticians, chemists, process engineers) working in synergy. One of the main fundamental objectives targeted consists of obtaining more accurate thermodynamics and mass transfer models in order to efficiently and reliably scale up advanced solvent systems, which offer the potential to bypass intermediate-scale testing.

Molecular modeling and simulation tools have advanced rapidly, so it is now possible not only to design both nonreactive and reactive absorbents from fundamental molecular principles, but also to redefine molecular design criteria through strategic placement and orientation of atoms [Cantu et al. 2016a; Cantu et al. 2016b; Malhotra et al. 2017]. This approach has been used to some extent in the design of nonaqueous and other alternative CO_2 capture systems (among many other systems [Septavaux et al. 2017]) in which the options for solvent composition, structure, and functionality are limitless. The space of solvent development efforts, especially at early TRLs, should not be restricted to aqueous solutions of molecular amines and will be expanded. Molecular modeling and simulation can be used to identify targets for experimental synthesis and testing and tailored process design and integration.

Throughout this development process, interactions with the chemical industry need to be established to determine whether the synthesis targets selected are rationale, scalable, and justifiable and to anticipate the maturation process. Solvents could be designed and optimized for each source of CO_2; each type of capture mechanism; each process configuration; and operating conditions, including simultaneous capture and utilization as key process intensification perspectives. Conversely, novel process configurations that integrate well with CO_2 transport, storage, and utilization need to be developed to exploit the best of these new high-performance solvent systems.

Technology Impacts

The research outlined will have a broad scientific impact and significantly advance the scientific understanding of solvent-based CO_2 capture processes. This in-depth understanding will lead to an accelerated, lower-cost, and lower risk pathway for novel solvent-based systems toward higher TRLs. Specifically, enhanced knowledge will be gained from integrated experimental and computational tool sets for the development of new solvent systems, confirmed by comprehensive experimental data, and modeling tools that allow projections of the performance advantages of novel solvent systems over the current state of the art.

Fundamental research to develop high-performance solvent systems will be instrumental in significantly reducing capture costs. The advanced solvent systems developed based on fundamental scientific understanding, using state-of-the-art improved molecular and thermodynamic modeling tools, will potentially lead to expedited tailor-made solvents for capturing CO_2 from a variety of different source streams. This will lead to lower costs and reduced risks and more rapid technology deployment. The fundamental understanding of novel solvent systems will also help broaden the selection of technologies applicable to a wider scope of CCUS applications.

The scientific impact can be summarized along four main themes:

1. **Improved understanding and tool set for new solvents and molecules.** Early TRL research for solvent-based CO_2 capture processes should be guided or supported by new tool sets (experimental and computational). Specific examples are high-fidelity predictive models of thermodynamic and transport properties of novel target compounds, and models to derive molecular composition from target solvent properties. Such tool sets will enable researchers to conduct better informed and more efficient research within and outside of the range of current solvent chemistries and process schemes. The process implications and environmental acceptability of novel solvents can be assessed at very low TRLs.
2. **Dissemination of knowledge of solvent chemistry and processes across the scientific community**. The chemical and physical target properties of solvents are critically linked with the process design and specific process features. This is particularly true if the goal is to develop novel step-out technologies rather than incrementally improve current process approaches. Widespread knowledge dissemination across the fields of molecular modeling, chemistry, materials science, and chemical engineering will enhance collaboration across these disciplines and help to promote CO_2 capture products as feedstocks for new applications.
3. **More accurate projections of performance at a given scale**. It is critical to develop more accurate performance models that can predict the performance of a CO_2 capture process based on early TRL data. Such research will enhance the possibilities for faster scale-up and maturation of promising novel solvent systems. Accurate, higher-fidelity models will lower the cost and risk associated with scale-up, potentially to the extent that certain scale-up steps may not be necessary—especially at the very costly pilot and large-pilot stages.
4. **Tailor-made solvents and separation processes for a range of specific CO_2 sources and downstream use of the CO_2**. The scientific understanding at the integration interfaces between the CO_2 source, the capture process, and CO_2 use will become increasingly relevant. Given the wide range of CO_2 sources for which capture might make sense, it will be critical for the scientific community to broaden their efforts toward a sound scientific understanding across these various applications. The research would develop a broader "upstream" understanding of CO_2-containing gas streams and the implications for solvent systems (in terms of, for example, their CO_2 levels, process conditions, contaminants). The research would also consider the downstream use of the CO_2, whether at the pipeline or other transportation system or use in integrated chemical conversion processes. We expect that this integrated approach will stimulate further innovation toward commercially relevant CO_2 capture implementation.

Conclusions

The technological needs in this area are solvents and associated processes that can capture CO_2 at a lower cost than first- or second-generation aqueous amine systems. Therefore, the scientific challenge is mastering the ability to accurately predict and then control the chemical and physical properties of potential liquid absorbents for CO_2 capture. Only scientifically diverse teams spanning from fundamental to applied science can provide the knowledge base that not only improves solvent performance but also learns *how* to improve solvent performance. The scientific impact of this research will be a new tool set for new solvent and molecule design that spans from atoms to process energetics. Such a tool set will be applicable to a variety of solvent chemistries and processes, providing more accurate projections of separation process performance at a given scale, tailor-made solvents and separation processes for a range of specific CO_2 sources and the downstream use of the CO_2, including onsite use.

2.5.2 PRD C-2: Creating Environmentally Friendly Solvent Processes for CO_2 Capture

Solvents for post-combustion capture experience losses due to oxidation, nitrosation, aerosols, and other contaminants and mechanisms that are not fully understood. These losses lead to significant environmental impacts and costs for solvent makeup and reclamation to separate impurities. This PRD will close this knowledge gap by systematic studies of contaminants and loss mechanisms that will be applicable to all solvents and all applications. The research should develop methods to mitigate solvent losses that will reduce the risk, cost, and environmental impact of deploying solvent systems for CCUS.

Scientific Challenges

The development and deployment of second-generation amine scrubbing for CO_2 capture has identified several unresolved challenges associated with the effects of flue gas contaminants on solvent losses (Figure 2.16). The known important effects on the solvent include oxidation by O_2 and dissolved iron, nitrosation by NO_2, and formation of solvent aerosols from SO_3 and fine ash. The products of these undesirable side-reactions impact the environment as gaseous emissions in the clean flue gas and liquid waste that must be disposed of. Additional costs are incurred for operations to reclaim solvent from the waste liquid and makeup to replace the lost solvent.

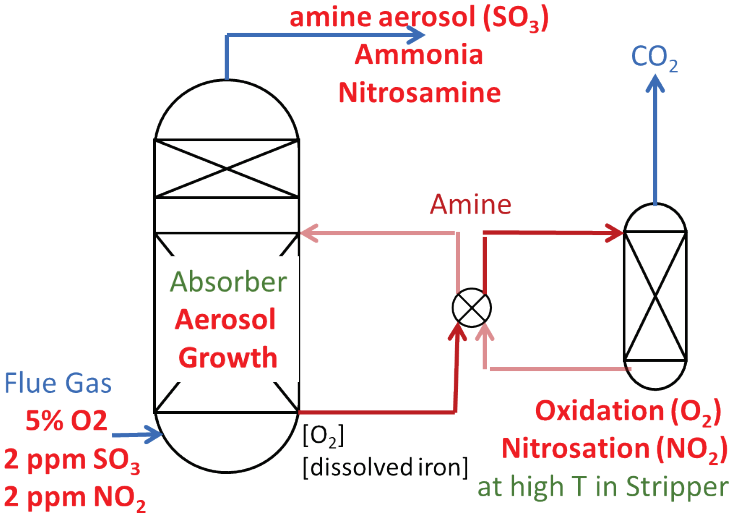


Figure 2.16. Contaminants that cause solvent loss and potential environmental impact. | Illustration courtesy of G. T. Rochelle, University of Texas–Austin.

The magnitude of these effects was discovered only as the second-generation technology was tested and deployed in long-term operation on real coal-fired flue gas. Laboratory-scale experiments have not been able to reproduce the magnitude and variability of these effects. Therefore, our fundamental understanding is insufficient to address these challenges. The development and deployment of a wider range of third-generation solvent systems in a wider range of industrial and power plant applications with additional contaminants may create additional challenges (Figure 2.17) in the form of side reactions or unexpected phenomena that may result in environmental impacts and solvent losses.

Our understanding of solvent oxidation is incomplete because it is a complex problem with many uncertainties. O_2 mass transfer often limits bench-scale experiments. Oxidation of aged amine inventory appears to be faster than oxidation of clean solvent. Oxidation and its catalyst (dissolved iron) increase with the accumulation of degradation products. Therefore, continuous reclaiming may reduce oxidation. Dissolved and entrained O_2 reacts with amine at stripper temperature in laboratory experiments. Foaming may accelerate oxidation. N_2 or other stripping of O_2 may reduce oxidation. Oxidation occurs at conditions of the stripper sump without dissolved O_2 in laboratory experiments. Therefore, minimum stripper sump temperatures and hold-up may reduce oxidation.

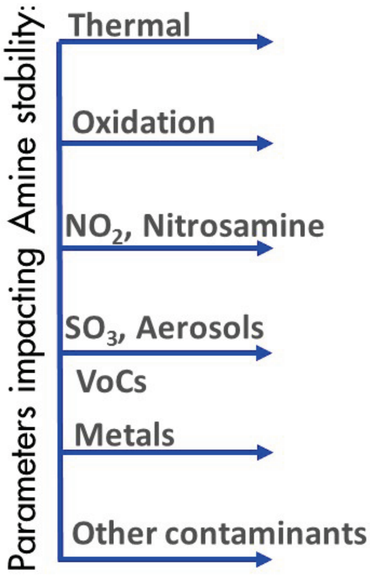


Figure 2.17. Parameters that impact amine stability.

In second-generation systems, SO_3, fine ash, SO_2, and other nuclei in flue gas result in the growth of amine aerosols (drops smaller than 3 μm) that are not collected. SO_3 can be eliminated by bag filters or gas/gas heat exchange. Episodic, unknown nuclei may be problematic. The severity of the amine aerosols will probably vary with amine volatility. An understanding is needed of aerosol growth and capture with a wide range of third-generation solvents and with unknown contaminants from additional applications that may provide nuclei for aerosol growth.

NO_2 in inlet flue gas oxidizes all amines and may also affect other solvent types. Secondary amines react to produce carcinogenic nitrosamine. Nitrosamine thermally degrades, resulting in amine oxidation products. NO_2 may be effectively minimized with selective catalytic reduction, scrubbing in the SO_2 polisher, or a bag filter with carbon injection. A systematic understanding is needed to predict the effects of NO_2 on all solvent types.

Research Directions

What does solvent loss mean? Solvent loss is the breakdown of the primary solvent to other compounds from exposure to O_2, high temperature, other gas components such as SOx and NOx, or metals from corrosion.

Understanding solvent loss mechanisms, the products formed, the potential for health and environmental impacts, and mitigation options for large-scale CCUS operation is a challenging task. It requires a combination of methods to

- Identify and quantify degradation components
- Mimic the degradation and emissions that may occur at large scale in the laboratory
- Develop systematic understanding of chemical mechanisms and emission mechanisms
- Develop models that allow reliable prediction of loss at large scale
- Identify and assess mitigation strategies

Amine losses and environmental impacts in second-generation systems

Identifying and quantifying the solvent degradation products and the contaminants that cause degradation requires a suite of analytical techniques able to identify and quantify ionic and non-ionic chemical species present in a complex matrix. New analytical methods need to be developed that are broadly applicable to the identification and quantification of components present in a concentrated matrix of organic species in both aqueous and nonaqueous environments (see the sidebar “Second-Generation Solvents”).

In addition to identifying and quantifying the components formed, understanding the potential health and environmental impacts of their emissions is crucial. This requires understanding the likely emission routes, environmental fates, and toxicity.

It is a multidisciplinary challenge encompassing the physics of emission and dispersion and the human health and ecological effects.

Contaminants should be identified and quantified in the full range of applications, including gas and coal-fired power plants, cement, steel, and refineries. Analytical methods need to be applied to quantify the solvent losses and environmental impacts in solvent pilot and demonstration plants operating with real flue gas with all applications.

Second-Generation Solvents

1. In a pyridinium chlorochromate process with second-generation solvents, CO_2 is liberated from the amine by heating in a stripper unit, typically at temperatures up to 150°C. Partially degraded amines can also be regenerated in a reclaimer unit in which high temperatures are used to purify the amines. However, the most common thermal reclaimer technology requires that the solvent be volatile, whereas a novel high-performance solvent system may have very low volatility, requiring specially adapted methodologies.
2. Second-generation amine solvents show greatly improved performance over first-generation solvents, particularly in terms of energy use, corrosivity, and degradation. These solvents usually combine at least two amines, one that enhances the kinetic rate of CO_2 absorption and one that allows the solvent to retain a high capacity of CO_2. These blends are often proprietary, and so their precise composition is uncertain.
3. Nitrosamines have been observed as degradation products in some amine-based processes. They are usually formed by the reaction of secondary amines with NO_2 and can be decomposed thermally.
4. Gas streams containing CO_2 can vary substantially depending on the original source. Levels of CO_2 vary considerably; for example, a typical flue gas from a gas-fired power station would contain 4% CO_2, whereas that from a coal-fired power station would contain around 12% CO_2. Higher percentages of CO_2 are also typical in industrial gas streams. The impurity profile will also vary substantially depending on the source and the clean-up methods used before CO_2 capture. All of these factors contribute to the complexity of the solvent degradation process.

Systematic chemical pathways

Careful laboratory experiments are needed to define the fundamental chemical and physical mechanisms of oxidation, nitrosation, aerosol formation, and other solvent loss processes. To understand the potential impacts at large scale requires knowledge of both the chemical mechanism and its associated thermodynamic and kinetic properties. Addressing this challenge is likely to require a combination of fundamental molecular modeling and systematic study of degradation mechanisms at varying conditions.

Solvent loss prediction and mitigation

Laboratory-scale experiments should be developed to fully represent the conditions and results of large-scale testing with real gas. Reliable prediction of losses in large-scale operation requires the development of small-scale methods to study loss processes that can reliably be scaled up. In concert with the need for improved experimental methods to study loss mechanisms is a need for models that describe both the chemical and physical processes involved in loss mechanisms. These models are a critical requirement if loss mechanisms are to be incorporated into process models able to predict loss and associated impacts at large scale.

It is only with this rigorous understanding of loss mechanisms that mitigation strategies can be developed. This is particularly relevant for new solvent chemistries that are likely to open up new opportunities for solvent reclamation and emission mitigation.

Technology Impacts

This research will provide the scientific basis of methods to minimize solvent losses and mitigate secondary impacts. The work will systematically identify solvent types that will be resistant to degradation and other solvent losses. Proper application of the mitigation methods will significantly reduce the cost of cleaning and replacing solvents. The scientific knowledge and experimental tools developed will be applicable to second- and third-generation solvents and to the wide range of expected applications for CO_2 capture.

Mitigating solvent loss and its impacts on the environment will enable the deployment of CCUS on a large scale by reducing uncertainty regarding those effects. Solvent loss management will minimize operating expenses by reducing the cost of solvent makeup. The understanding developed will be applicable to both second- and third-generation solvent technologies.

2.5.3 PRD C-3: Designing Tailor-made Sorbent Materials

CO_2 capture processes based on sorption/desorption of gases by solid materials have the potential to significantly reduce the energy penalty and equipment costs compared with state-of-the-art CO_2 capture technologies such as amine scrubbing. These processes can be divided into three groups based on different mechanisms: physical adsorption/desorption of CO_2, chemical absorption/desorption of CO_2, and separation of O_2 by oxidation/reduction. These categories use different types of materials and operate at different conditions (i.e., temperature, pressure, atmosphere). The ability to better design solid materials based on nanoscale insights has made major advances in the past decade. With increasing knowledge exchange between materials discovery and process development, classes of materials previously viewed as exotic are now viable at demonstration scales. Systematic materials improvement is an iterative process when multiple interrelated performance variables exist (Figure 2.18).

Scientific Challenges

Designing and constructing tailor-made materials for specific applications

It is common to seek a single critical metric to rank the potential of a material within a carbon capture process; but in fact, properties such as CO_2 uptake capacity, CO_2 selectivity, stability, and the energy needed to regenerate the material are interrelated and improving one often compromises another. For some adsorbents, adding molecular features that are strongly attractive for CO_2 increases the regeneration energy and may also increase water affinity. A critical challenge is balancing the different requirements in a single particle. The design of desired properties for an ideal carbon capture material begins at the nanoscale and must be informed by the process requirements.

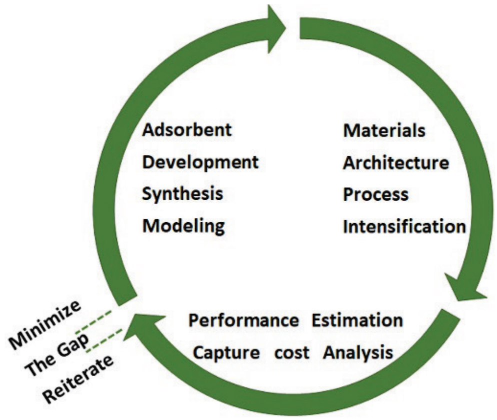


Figure 2.18. Adsorbent screening protocol. | Image courtesy of Soheil Kiavi

Understanding structure–properties relationships

Predicting CO_2 sorption in physisorptive materials extends beyond the interactions of the gas with the surface to the interactions of the CO_2 molecules with one another. There are subtleties of pore size and shape that are critical to CO_2 capture performance in the system, and the importance of understanding them is compounded with mixed gas streams. Advances in modeling have been significant; but there are still materials whose CO_2 capture properties elude accurate modeling, as existing models often do not mutually account for both thermodynamics and kinetics. Simulating mixed and wet gas sorption is critical and in the very early stages. The molecular form of a new material must be incorporated into the engineering process; doing so requires a physical transformation of the material into a microstructure to permit large flows of gas and energy (heat and mass transfer). A challenge is to retain or improve the intrinsic properties of the material in the processed form based on an understanding of the interactions at the interface between the solid particles themselves and with any supporting phase. Advanced in situ studies of these interactions under process conditions are needed. Each material and process will have an ideal complementarity with respect to structured forms.

Enhancing long-term reactivity, recyclability, and robust physical properties of materials in working cycles

Ultimately, material performance is dependent on the synergy between the molecular-scale features and the microstructured forms. This performance must be sustained, and the ability to design chemical, physical, and mechanical durability from a molecular scale in a potentially multicomponent material is a significant challenge. It encompasses the ability to survive many working cycles, resistance to reaction with gas impurities, and stability during plant startup and shutdown.

Research Directions

Deploying a comprehensive approach to evaluating gas–sorbent interactions

For physical adsorbents, it is critical to understand the molecular features that enable a balance of capture requirements, predict realistic structures, and develop synthetic routes to such new tailor-made materials. For any of the sorbent materials, we must develop means to better understand the formation of a product (i.e., a carbonate) layer on the surface and the diffusion mechanisms through the products, which are affected by the presence of other species (e.g., water vapor, sulfates, additives). For chemical looping combustion, we must develop means to better understand the impact of structural change on cation diffusion, as well as the recrystallization effect during redox processes. We must develop better tools for in situ monitoring at the nanoscale to better design materials.

Understanding the effects of impurities and water on chemical stability and performance

For adsorbents, experimental and computational tools are needed to screen accurately for co-adsorption in mixtures of wet gases and iterate the findings with materials design and testing. For calcium looping, accomplishing this means understanding—ideally, via in situ analysis— how sulfate formation affects particle structure and reactivity, as well as the effects of minerals from ashes. For chemical looping combustion, it means making materials resistant to forming carbonates, sulfates, and hydroxides that reduce the performance of the oxygen carriers and may be detrimental to mechanical stability.

Improving current tools to quantify mechanical properties

For adsorbents, there is a need to transition potential breakthrough materials into structured forms and carry out process tests. Doing so will require more facilities to carry out process-level testing on a small (subkilogram) scale to accelerate the discovery/testing cycle. For calcium looping, there is a need to develop standards for quantifying attrition and fragmentation of particles at high temperature under cycling conditions. For chemical looping combustion, ways to assess mechanical strength under both reducing and oxidizing conditions at high temperature should be sought. Improved assessment methods will aid understanding of the changes in strength related to phase changes in materials, which affect the attrition and crushing strength under fluidized and fixed bed conditions.

Understanding composite structure and the thermal and chemical interactions between materials

This point is common to all three technologies and relates to understanding the gap between the nanoscale and the microscale. Techniques to probe average structures are not adequate to understand the roles of interfaces and structural defects in evolving processes.

Technology Impacts

Solid sorbents and looping technologies can offer lower-cost carbon capture through both lower energy requirements and facilities that will have a smaller footprint with lower capital cost. For maximum impact of breakthrough materials, the ideal route is not to retrofit existing infrastructure but rather to optimize the unique features of materials at different scales of development for specific processes. This approach is pragmatic, as it will also permit aligning materials with their ideal processes. It extends well beyond the scope of adsorbent and looping systems, as materials and knowledge gained from these fundamental studies will transfer to membrane science and beyond. With respect to a smaller footprint, a key opportunity created by new capture infrastructure is not simply the provision of CO_2 for a utilization/conversion process but actual process integration to enable another order of process efficiencies. The combining of CCUS technologies can occur even at the microstructural level. For many energy-intensive gas separations involving CO_2 or relating to CO_2 emissions, there is tremendous scope and opportunity for step-change technologies.

Conclusions

Emerging classes of materials and nanoscale insights into materials design, derived both experimentally and computationally, have created new opportunities for solids in gas separations. For maximum impact, materials must be assessed from the nanoscale upward, and synergies with modern engineering processes and advanced testing and manufacturing must be recognized and exploited.

2.5.4 PRD C-4: Integrating Sorbent Materials and Processes

Carbon dioxide capture processes based on solid sorbents with improved material properties, process configurations, and reactor concepts can lead to energy, infrastructure, and cost efficiencies. Achieving these efficiencies necessitates a fundamental understanding of the requirements of the materials for a specific process and of the relevant transport phenomena. In particular, to realize the potential of the capacity to tailor-make materials, it is important that all requirements be included at an early stage of research. Therefore, these processes, together with the related reactor concepts and materials, should be developed synergistically to minimize CAPEX and OPEX.

Scientific Challenges

Carbon dioxide capture based on sorption/desorption of gases by solid materials can significantly reduce the energy penalty and equipment costs compared with capture technologies such as amine scrubbing. For adsorption-based processes, this potential relates to reduced energy requirements for desorption and lower CAPEX due to process intensification. For high-temperature absorption processes, reducing energy and cost requires highly efficient heat utilization (e.g., for added power generation). For chemical looping, this depends on separating O_2 and N_2 without additional energy. Although the feasibility of these processes has been proved through intensive laboratory and pilot testing, there is much potential to further enhance performance by improving material properties and reactor concepts. Examples of the challenges of the different processes are

- Conventional pressure swing adsorption processes are expensive because of high compression costs. Conventional temperature swing processes suffer from large footprints and high CAPEX due to their slow cycle rate. The footprint of a temperature swing process could be drastically reduced by employing a rapid cycle process combined with structured adsorbent beds.
- The energy penalty of high-temperature absorption processes (such as calcium looping) is mainly due to the need for high-purity oxygen with the calciner. The energy needed and associated costs can be reduced by new process concepts that avoid oxy-combustion (e.g., indirect calcination) and by improved sorbents with high CO_2 capacity. There is also potential for combinations of calcium looping and chemical looping combustion.
- A major challenge of chemical looping combustion is the full conversion of the fuel in the reducer, particularly when solid fuels are used. This issue can be addressed by novel reactor concepts that improve gas–solid contact and/or by materials with the capability to release molecular oxygen. Elevated pressure can also assist in higher conversion.

To address these issues, it is essential to understand the relationship between material and process integration to produce optimal capture designs for flexible operation, thereby bridging the gap between process engineering and materials science. Furthermore, it is important to gain improved understanding and control of hydrodynamics, heat and mass transfer, and integration with novel (potentially intensified) process and material design. Doing so opens the possibility of “redesigning CCUS from the ground up,” especially with the emergence of new solid sorbents.

Research Directions

The following research areas, including some process-specific examples, are proposed to address the challenges.

Understanding the intrinsic reactivity and physical strength relationship of sorbents

For fluidized bed–based processes, it is imperative to determine how mechanical strength and degradation interrelate. New methodologies are needed to understand this critical combined factor over sustained reactor and sorbent tests. This understanding is crucial for achieving sufficient lifetimes and for keeping OPEX low.

Adapting sorbents, processes, and reactor/contactor configuration for high- and low-temperature operation

Adsorbent screening test protocols are needed for ranking performance in carbon capture applications. Among key properties to be studied are resistance to moisture and contaminants under operating conditions, selectivity, and kinetics of sorption and desorption. These properties can be cross-correlated to capture cost by a methodology combining simulations and testing data for an optimized process (e.g., rapid cycle temperature swing adsorption, Figure 2.19).

The deployment of novel calcium looping processes with indirectly heated calciner configurations opens the door to next-generation materials with longer lifetimes (which could make more effective but expensive materials, such as supported or doped sorbents, viable). In this case, an optimum will exist that balances OPEX due to material production, OPEX due to fuel consumption, and CAPEX due to reactor size. For chemical looping, the thermodynamic properties of the redox material determine the operational temperature and pressure window. Hence, development of materials and processes goes hand in hand.

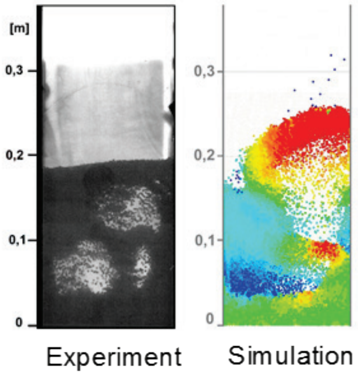


Figure 2-19. Photograph and calculated particle distribution of a quasi–2D fluidized bed. | Image courtesy of Technische Universität Darmstadt

Developing comprehensive computational models to aid design of integrated, flexible capture processes.

In fluidized bed processes, advanced models are required to accurately predict the interaction of momentum, heat, and mass transfers in the complex flow structures (bubbles, clusters) of the gas/particle flow. Developing these models necessitates a multiscale approach to capture all relevant length scales (from particle to flow structure to equipment level) and time scales (from fast kinetic gas phase reactions and particle collisions to slow gas–solid reactions and particle circulation between reactors).

Developing novel equipment and cycle designs

To operate in rapid cycle regimes, the transport phenomena of adsorbent beds must be intensified. Appropriately structured adsorbent beds will reduce the pressure drop, enhance mass and heat transfer throughout the bed, and help to intensify the separation by rapid cycling. Such systems need to be optimized with regard to conversion efficiency and equipment size. Coupling this need with the emergence of new materials, small-scale pilot testing opportunities are needed for adsorbents before larger deployment.

For indirectly heated calcium looping, the heat exchanger must provide high heating rates in a compact design (e.g., heat pipes in dense fluidized beds or circulation of particles). For integrated CO_2 capture by calcium looping from industrial applications such as cement manufacturing, new reactor concepts (e.g., entrained flow reactors) may be required to manage the particle properties of, for example, the cement raw materials. All these concepts must be optimized with regard to conversion efficiency and equipment size. In chemical looping combustion of solid fuels, new reactor types, such as multistage fluidized bed reactor configurations, offer significant improvement of the fuel conversion in the reducer. To develop such novel systems requires both cold flow testing to understand the hydrodynamics, and hot testing to evaluate the conversion efficiency of char, volatiles, and gasification products. The CAPEX of chemical looping systems could be reduced by pressurization, which calls for investigations under pressurized conditions.

Technology Impacts

The processes described hold promise to significantly reduce the energy penalty and CAPEX for CCUS implementation by employing novel advanced cycles to exploit next-generation materials, combined with reductions in environmental impact and corrosion risk. These processes have high potential to provide solutions for flexible operation. Advanced cycles can efficiently integrate with CCUS opportunities in the context of gasification, reforming, and chemical syntheses. Fundamental understanding and design of high- and low-temperature and high- and low-pressure processes is fundamental and extends to applications beyond CCUS (e.g., power, steel). Improved understanding of and models for heat and mass transfer and hydrodynamics will lead to improvements in performance, safety, and reliability. Ideal matching of materials with processes will offer benefits to many applications.

Conclusions

Carbon dioxide capture processes based on sorbents offer increased energy efficiency and reduced OPEX and CAPEX. Further research in integrated process and material development must synergize to reap the benefits of these technologies. This approach includes intensive testing at real conditions, as well as the development and validation of comprehensive models for process and reactor design. This PRD should enable the design of efficient pilot-scale test facilities with improved processes under real conditions.

2.5.5 PRD C-5: Understanding Transport Phenomena in Membrane Materials

During the past decades, novel high-permeance materials have emerged which could have a significant impact on membrane performance. However, because nonclassical materials are being used, the current know-how on mass transfer must be improved to enable the design of cost-effective membranes. Therefore, it is important to investigate the transport behavior through these materials by using detailed characterization and molecular modeling approaches.

Scientific Challenges

Currently, commercial gas separation membranes are made from glassy or rubbery polymers, often largely amorphous, that operate based on the solution-diffusion model [Wijmans and Baker 1995]. They have broad free volume distributions and relatively nonspecific interactions between gas molecules and polymer segments. These characteristics contribute to poor combinations of permeability and selectivity [Park et al. 2017] that fall well below the empirical Robeson perm-selectivity trade-off. Emerging materials for CO_2 capture membranes, such as thermal rearranged polymers (TRs), polymers of intrinsic microporosity, carbon molecular sieve (CMS) membranes, mixed matrix membranes employing MOFs, zeolites or other nanoparticles, and FTMs have been developed in recent years to improve permeability and selectivity. Although the basic mechanism of mass transport in such emerging systems is well understood, there is a striking lack of detailed understanding and correlative or predictive models of multicomponent transport (i.e., transport of multicomponent gas mixtures). This deficit hampers the ability to predict, for example, membrane performance in realistic multicomponent mixtures, based on pure gas permeation experiments that make up the bulk of the available information regarding membrane performance [Liu et al. 2016].

Naturally occurring membranes, such as ion channels and aquaporins, have exquisitely narrow pore size distributions, interactions specifically tuned to transport the species of interest, and extremely thin structures (<2 nm), resulting in extraordinarily high combinations of permeability, flux, and selectivity [Koros and Zhang 2017]. Next-generation materials (e.g., MOF nanocomposites, TRs, polymer-derived CMS membranes) are designed largely based on efforts to narrow and tune pore size distribution in porous or semi-microporous materials. Fundamental understanding of the mass transport mechanism (i.e., how similar to or different from the classical solution-diffusion picture it is) in such semi-microporous materials is at a very crude level. In such materials, differences between pure and multicomponent gas mixture properties can vary by more than an order of magnitude; and no quantitative, predictive models are available [Liu et al. 2016]. Developing a fundamental understanding of multi-component transport in such systems is thus critical to advancing materials design for future membranes. FTMs—based on highly specific chemical-based interactions of the membrane with a component of interest to promote both high permeabilty and selectivity—are promising, although long-term stability needs to be addressed further. Better understanding of mechanisms to arrest possible carrier degradation in FTMs could open the door to dramatically improved membranes for gas separations.

The knowledge of transport in inorganic membranes, either dense or microporous, has over the years developed through continuous improvements in modeling and characterization tools and the ability to make controlled membrane structures at the nanoscale. In particular, the understanding of membrane flux in well-defined lattices is based on good theoretical and experimental evidence. Less is understood about how point defect clustering and line and interface defect regions affect transport properties. Only recently have charged core regions and space charge regions at interfaces like grain boundaries and surfaces become better understood. More advanced simulations are necessary to develop an understanding of the energetics and dynamics of transport processes across and along 2D interfaces such as dislocations, grain boundaries and external surfaces, and 3D defects such as extended point defect clusters, defect ordering, and domains of heterophases on the nanoscale. In microporous systems, which can be either amorphous or crystalline, the internal surfaces rule the interactions with the permeating gas-phase molecules. Possible affinities resulting in pore condensation and preferred permeation pathways can lead to increased permeability and selectivity; a deeper understanding of these affinities is needed to allow the maximum use of these types of membranes.

Mechanistic models may not only describe the transport of the preferred transported species, like proton and oxide ions, but also form the basis for understanding slower processes such as cation diffusion in dense ceramic oxygen and hydrogen separation membranes. Understanding this behavior is essential to describing central degradation processes like creep and kinetic demixing that are important in determining the lifetimes of membrane devices. Improved understanding of interfaces is also important for hydrogen-selective metal membrane flux and stability. Their surfaces are vulnerable to many components, which can reduce flux; and their grain boundaries appear to be instable, creating regions with voids after extended operation.

Research Directions

Better predictive tools linking membrane structure to membrane separation properties are needed. They will enable the use of next-generation membranes for CCUS applications,. As high-performance computing capabilities continue to evolve, the ability to describe and understand transport at the molecular level through various membrane materials continues to improve. For example, classical molecular dynamics simulations can be used to examine the dynamics of molecular motion at the interface and through the bulk membrane. However, there currently is poor understanding of the transport of targeted gas species through next-generation membrane materials, such as mixed-matrix membranes, in which interfaces are important. Consequently, novel computational methods that accurately describe the transport of gas molecules are needed to rationalize the experimental data obtained and predict new materials or structures with tailored properties for specific separations.

Interactions between the interfaces and moving species must be better understood through fundamental research. This applies to microporous membranes, as well as to dense inorganic membranes. In particular, increased understanding of transport along and across interfaces of the highly diffusing species is needed to improve membrane selectivity and flux. More attention also should be given to the slower-moving species that are important for slowly changing membrane properties. Slow transport often determines the membrane robustness and practical lifetime during operation. To obtain improved understanding and better membranes, fundamental modeling and simulation of transport property–structure relations are required—particularly for interfaces and domains of extended defect structures that deviate from well-defined lattice descriptions. Further studies of interactions between the surface and gas molecules, and their effect on transport, are required. Examples of such gas–surface interactions are surface poisoning, adsorption or pore blockage of competing molecules, size exclusion, molecule splitting, and recombination and segregation of components.

In all cases, a deep knowledge of membrane behavior in an operative environment and of the influence of the module, the reactor, and the system around the functional device are critical to enable effective separations and reduce limitations due to gas phase diffusion.

Technology Impacts

A better understanding of the transport mechanism in emerging membrane materials can translate into better overall membrane performance (e.g., permeance, selectivity) in system operation. The costs of CO_2 capture fall into three main areas: energy consumption, depreciation of the rotating equipment, and membrane skid depreciation and membrane replacement. Doubling the membrane permeance could mean halving the membrane cost contribution, which could be approximately 15% of the overall capture cost. Higher selectivity could also result in savings in power consumption.

Understanding of the transport phenomena associated with components such as CO_2 and H_2 through next-generation materials, such as oxides and mixed-matrix materials, can as well be directly applied in the development of adsorbent-based processes. The same types of phenomena that occur in membrane processes also occur in adsorption-based processes (i.e., adsorption and diffusion).

Conclusions

Molecular-level understanding of mass transport phenomena is critically needed to advance next-generation membranes to industrial application. This knowledge, which will lead to the development of highly permeable and highly selective next-generation membrane materials, will be enabled by advanced characterization and molecular modeling,

2.5.6 PRD C-6: Designing Membrane System Architectures

Next-generation materials can lead to robust, cost-effective membranes. However, significant effort is needed to direct the processing of these materials toward robust, high-permeance membranes for cost-effective, energy-efficient process designs.

Scientific Challenges

The process of converting a novel, next-generation material to a commercially viable membrane module (see Figure 2.20) useful in CCUS applications is a critical step that often becomes mired in the commercialization "valley of death" for promising new membrane materials. For high productivity, typically membranes are currently fabricated as either (1) composites comprising a thin layer deposited on a porous support, (2) monolithic structures with asymmetric (skin/substructure) morphology, or (3) a composite asymmetric layer on a porous support. The mechanistic lack of understanding of the fabrication process, and specifically the interface between separating layer and support structures, hampers our ability to translate novel membrane materials into high-performance membranes. The challenge in making a thin, defect-free selective layer is twofold:

1. The fabrication method must be appropriate for large-scale manufacturing of extremely thin, defect-free selective layers.
2. The support substructure/morphology must support the desired stable, integral selective layer but not limit the composite membrane performance.

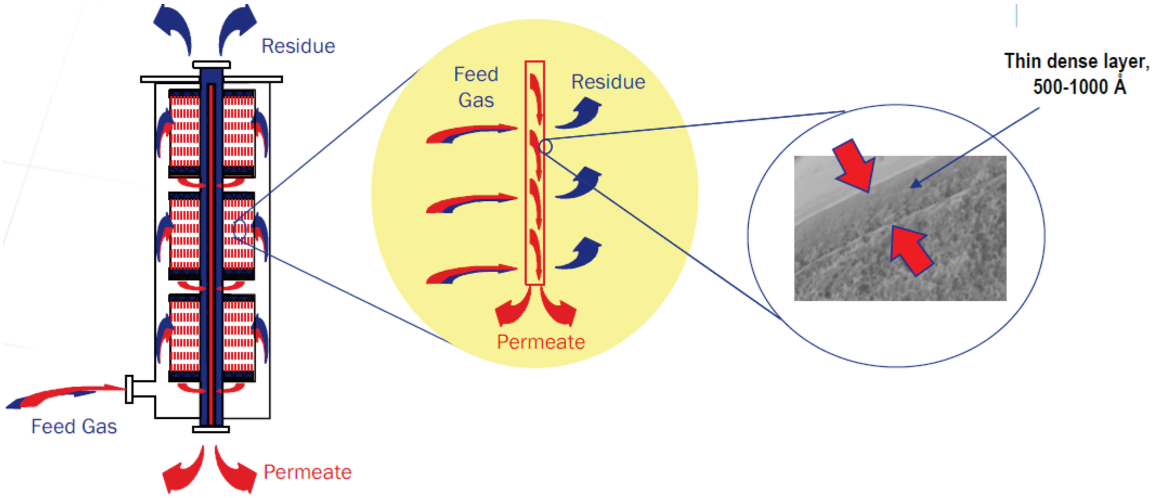


Figure 2.20. Illustration of technology development from promising polymer candidate to asymmetric composite hollow fiber packaged in multi-module configuration. | Image courtesy of Air Liquide Advanced Separations

The fundamental research to establish both (1) and (2) and manufacturing concerns about subsequent membrane upscaling and module integration are rarely considered at the laboratory stage. However, innovative ideas are needed to shorten the path from fundamental development of new membrane materials to highly performing membrane modules. Low-cost thin film synthesis techniques enabling the preparation of large, high-quality membrane surface areas on appropriate supports (shape, pore structure, stability) need to be developed to produce improved membranes.

A further challenge is the manufacturing concerns and hydrodynamic considerations for converting promising membrane performance in the laboratory to usable modules. The identification of next-generation ultra-permeable, highly selective materials will make these challenges even more difficult but at the same time increase the payoff for overcoming them. Next-generation materials also expand the possible window of membrane operation, raising the possibility of novel process designs. The optimum stage, in terms of realism and cost, at which to validate membrane robustness at the conditions envisaged in novel process concepts, is the later stages of the membrane development step.

Research Directions

Development of higher-porosity, high-permeance, and high-surface-area supports needed for the final composite/asymmetric membrane is critical. Understanding of the structure and transport of selected gas species through the support—as well as the interface between the highly permeable, selective material and the support—will also play an important role in improving the performance of the module. In addition, one must also consider manufacturing techniques to produce these membranes that are feasible at large scale. Currently, membranes and membrane modules are developed mostly for high-pressure applications (CO_2 capture from high-pressure natural gas, hydrogen from syngas). Post-combustion CCUS applications are relatively low-pressure applications in which ultra-high-permeance membranes are needed. For both high- and low-pressure applications, suitable membrane materials are emerging; however, the support resistance degrades the overall performance when the materials are fabricated into thin membranes using current technology.

Radically different approaches to create innovative membranes and membrane modules will lead to lower capital cost and lower energy requirements of the capture plant. A common drive seen in membrane science is to pack as much of the membrane surface area as possible into a single module. This practice has led to the development of hollow-fiber and spiral-wound membrane modules. Minimizing parasitic pressure drops and optimizing concentration profiles are key concerns in module design for exploiting the ultra-high permeance and selectivity of next-generation materials.

Expanding the range of operating conditions by enhancing membrane stability would allow the use of new process concepts. Next-generation materials also expand the possible window of membrane operation (e.g., temperature, pressure, contaminant resistance), raising the possibility of novel process designs. This could lead to a significant improvement in energy efficiency, for instance, by enabling operation at higher temperatures. Inorganic membranes, such as dense ceramic proton conductors or ceramic-molten carbonate dual-phase membranes, can sustain high temperatures and show high selectivity. However, the current materials require higher temperatures to provide useful fluxes. One example of a promising application is integration of a dual-phase CO_2-selective membrane [Wei et al. 2015]. Another concept aims at replacing gas turbines on offshore rigs with fuel cells and membranes to increase energy efficiency and cut emissions [CMR Prototech 2017].

Technology Impacts

More robust and efficient membranes and membrane modules will enable the integration of next-generation materials into novel process designs in many different markets, such as oil and gas, maritime, sea farming, and agriculture. Advances in membrane and module fabrication technology are key to facilitating process integration and a shorter time-to-market for novel designs. They will also have a positive impact on the capital costs and operating costs of membrane-integrated CCUS systems in general. Understanding the structure–property relationship between the support and the overall membrane performance, as well as the interplay between the support and the selective layer, will enable a near-term impact on membrane module performance. And it will allow greater predictability in designing new membrane systems with next-generation membrane materials.

Conclusions

It is of crucial importance to develop scalable methodologies for producing membranes. Next-generation membrane materials are currently being investigated. To be able to harness the potential of these materials, significant improvement is needed in manufacturing high-performance membranes and in improving membrane modules and process designs.

2.5.7 PRD C-7: Catapulting Combustion into the Future

Combustion has progressed over centuries by encompassing a wide range of reaction kinetics, heat transfer, hydrodynamics, flame dynamics, and materials science. Despite the maturity of the field, advances in science provide the opportunity to further enhance combustion system performance at elevated pressures to achieve zero emissions through CCUS. In the past few decades, high-pressure combustion science has led to significant performance improvements for internal combustion engines and rocket motors and offers great potential to increase the efficiency and reduce the size and cost of utility- and industrial-scale combustors.

Fundamental research to develop robust understanding and models of these complex processes in high-intensity pressurized combustion will lead to transformative breakthroughs for a wide range of industrial and power generation combustion-related processes that emit no CO_2.

Scientific Challenges

Combustion is the heart of fossil fuel–based electric power generation technologies and many industrial processes. Although the thermodynamic and chemical foundations for the equilibrium reaction of a given fossil fuel with a suitable oxidant are well understood, design of actual hardware operating at extreme conditions and within very short time scales still requires extensive testing and proprietary empirical correlations. To achieve rapid development of high-pressure combustion technology it is necessary to move toward a mechanistic design approach based on chemistry and physics in combination with validated models.

In one sense, scientific challenges associated with combustion at high pressures (i.e., up to 300 bar) with any type of oxidant or fuel are not too different from the challenges at present with gas turbines, boilers, and rocket engines. Largely, conventional combustor and burner design is based on extensive data obtained from full-scale experiments and field operation of existing hardware, which are distilled into empirical design. However, even though designers are armed with proprietary knowledge and design tools, combustors operating at extreme conditions still require “tuning” before commercial operation.

Zero-emission high-pressure combustion technologies are envisioned to proceed under extreme conditions with pressures up to 300 bar and localized temperatures up to about 2500°C in combination with highly reactive species. The reaction spaces are characterized by extremely high reaction rates with varying flow fields. Consequently, it is quite difficult to obtain data to characterize these systems. Obtaining data is complicated by the potential presence of solids, liquids, and vaporized inorganic species that may condense on device surfaces. Because of the small sizes of the combustion systems, intrusive instruments can disturb and even react with the region of interest.

Often, combustion models are developed under the assumption that the modeling parameters are perfectly known; however, in practice, there is uncertainty in the values of the parameters because of measurement errors, complex interactions among various phenomena, and transient effects. In modeling and developing high-pressure combustion technologies, it is important to consider and monitor uncertainty to evaluate and reduce development risk. Doing so will provide guidance in identifying data that are crucial to the successful implementation of models.

Research Directions

Models validated against experimental data are requisite for the design of reliable high-pressure combustion systems; in particular, for systems using purified oxygen as the oxidant with various fuel impurities. Model validation in turn requires a good understanding of reaction kinetics at high pressures and near-stoichiometric conditions. As pressure increases, three-body reactions increase in rate faster than two-body reactions. Therefore, a better understanding of three-body collision reaction mechanisms involving species such as radicals and ions should be sought for modeling of high-pressure combustion processes. Such models, combined with experimental data will lead to better understanding of the speciation and fluid dynamics of the combustion zone for the design of fuel injectors (burners) and combustors with good stability.

Developing novel high-temperature, high-pressure cycles that enable efficient CO_2 capture will require instrumentation capable of probing high-intensity combustion regions. Nonintrusive techniques for experimental investigations must be used to gather data without disturbing the experiments, e.g., capacitance of x-ray tomography.

Instruments will be required to

- Determine gas and solid composition in 3D volumes, including not only bulk materials but also trace constituents that may foul or damage downstream processes—e.g., sub-micron solids that may contain heavy metals.
- Measure material and heat flux in multiple dimensions in potentially optically dense systems containing particulate material.
- Measure combustion acoustics to ensure that the systems can be started, operated, and stopped without damaging the equipment. This is required not only within the combustion space but also in connected systems such as heat exchangers and turbomachinery.
- Measure operating conditions, including temperatures, throughout the reacting flow fields and over surfaces at high data rates.

Research is also needed to develop high-pressure flue gas cleanup techniques to remove impurities such as sulfur oxides (SOx), nitrogen oxides (NOx), particulate matter (PM), and trace constituents. Simplified flue gas treatment due to reactions that proceed rapidly at high pressure encourages global deployment with a wide variety of fuels; however, development of many of the treatment steps is at an early stage. A thorough understanding must be developed of the composition of water removed from the flue gas stream and waste streams with regard to impurities it contains, its removal and disposal, and other treatment issues for all potential fuels and oxidants.

Opportunities for CO_2 conversion via chemical and biological processes should be evaluated in conjunction with high-pressure combustion, since a number of the requisite feedstocks are produced and captured, i.e., water, sulfates, nitrates, and of course the CO_2. The potentially negative effects of low pH and heavy metals must be considered as these opportunities are evaluated.

In addition to natural gas (methane), potential fuels such as coal, syngas, biomass, ammonia, and formic acid should be investigated for use in high-pressure combustion. In the case of biomass, it may be possible to remove CO_2 from the atmosphere on a net basis, assuming that biomass is carbon neutral; this should be confirmed and maximized via life cycle assessment.

For robust combustor design with acceptable life cycle cost, research into high-pressure corrosion, slagging, agglomeration, and fouling mechanisms is requisite. This should lead to appropriate mitigation methods and materials. Thermodynamic databases required for developing mechanistic models required to address these problems are incomplete and should be further developed, since some constituent interactions are very poorly understood.

High-pressure oxy-combustion technologies will greatly benefit from integration with low-cost oxygen production techniques, such as ion transport membranes (ITMs). Consequently, reliable, high-temperature and high-pressure, robust, scalable ITM technology development would be highly beneficial. This requires research into challenges associated with differential expansion, unsteady state transients such as system startup and shutdown, and resistance to fouling and poisoning. Selected ITM materials with complex structures must be amenable to mass manufacture; i.e., membranes must be available in appropriate quantities for commercial deployment.

Because of the small sizes of many of the components of high-pressure combustion systems, additive manufacturing will be well suited to rapid construction of equipment. Pre-prototype components and laboratory devices should be created through additive manufacturing techniques to allow experimental systems to be developed rapidly and modified on an as-needed basis, using the construction methods that will eventually be used in commercial products.

Technology Impacts

The key benefits of high-intensity pressurized combustion for CCS are

- More efficient heat and power production compared with low-pressure technologies
- Easy removal of impurities produced by a wide range of fuels (e.g., SOx, NOx, heavy metals) from the flue gas
- Capture and reuse of water produced during combustion, instead of venting
- No large chemical inventories
- Small system footprint
- Breakthrough reductions in capital and operating costs
- Potential for retrofit when low-carbon feedstocks, such as ammonia and hydrogen, are used

Improvements in thermodynamic databases related to fuel ashes will address knowledge gaps in industries such as metals production and ceramics production, allowing progress in advanced materials development and improved efficiency during manufacture.

Progress in high-pressure combustion modeling from atomic scale to system-wide scale, and the formulation of new materials for extreme conditions, will complement research needs and advances in aerospace, resulting in increased efficiency and reduced costs for both atmospheric and orbital applications.

Conclusions

Combustion is arguably the oldest field in chemistry and physics. Yet high-pressure combustion remains a relatively unexplored area, with enormous potential for capital and operating cost reductions, that has hitherto largely been the domain of experimental rocket scientists. Fundamental research to develop robust understanding and models of these complex processes could lead to transformative breakthroughs for a wide range of industrial and power generation combustion processes.

Considering its significant potential for carbon-free, efficient power generation from fossil fuels, there is a real need for fundamental research into combustion at high pressures, with oxygen or any other oxidant, with natural gas and other fuels (e.g., hydrogen, ammonia, formic acid).

2.5.8 PRD C-8: Producing Hydrogen from Fossil Fuels with CO_2 Capture

Technologies such as integrated steam reforming/catalytic combustion microchannel reactors with CO_2 capture or chemical looping reforming (CLR) offer interesting alternatives to water-splitting technologies for production of carbon-free H_2. These also offer scope for integrating a range of other capture and separation technologies for CO_2/hydrogen, such as cryogenics and advanced membrane components. These technologies would enable integration and process optimization schemes that would further reduce hydrogen production costs and be viable in a wider range of hydrogen production unit sizes.

Scientific Challenges

Fossil fuel–based hydrogen production with CCUS is essential to provide the large amounts of low cost, low-carbon hydrogen that will be needed as a fuel or feedstock in the transition to net zero emissions. It is critical that innovation in appropriate types of zero-emissions H_2 production be driven in parallel with ongoing initiatives to use H_2 to displace carbon-based fuels in heat, power, industry and transport. Current H_2 steam methane reforming production technologies are not well suited to full CO_2 capture. Conventional thermal and catalytic partial oxidation techniques for H_2 production have intrinsic advantages for CO_2 capture, but they currently require that O_2 be supplied from air separation units that are expensive to build and operate and viable only at larger unit sizes.

A combination of advanced materials and novel processes will be required to produce low-cost hydrogen via capture and storage from a range of fuels. The following are the most important challenges:

- Suitable materials are required for novel hydrogen production systems, such as catalytic microchannel reactors for reforming or oxygen carrier materials for CLR:
  - Reliable, high-temperature and high-pressure, robust, scalable materials
  - Long-term mechanical integrity
  - Non–steady state transients/startup/shutdown
  - Resistance to fouling, poisoning, coking, and so on
  - Configurations that offer a route to mass manufacture
  - Complex material formulation (all materials need to be available in appropriate quantities)
- Microchannel and other types of reactors must be suitable for use as part of a high-temperature reactor, notwithstanding differential expansion due to variations in temperature and/or oxygen concentration.

Research Directions

Advanced combustion-based technologies are emerging as enablers of hydrogen production. New, improved techniques for integrating combustion, such as microchannel reactors, offer great potential to improve the performance and cost of hydrogen production. Progress in combustion and partial-oxidation applications is becoming more feasible owing to new laboratory techniques for probing combustion reactions and improved modeling capabilities. In addition, new additive manufacturing techniques offer scope for novel geometries in all components.

Reforming with oxygen supplied via high-temperature membranes and integrated with hydrogen production is an area in which lower-TRL fundamental research activities are critical in achieving breakthroughs. Linking combustion and reforming in microchannel reactors also offers significant scope for cost and performance improvements, particularly for distributed hydrogen production.

Fluid flow and mixing in microchannel reactors is laminar in nature, allowing predictable and finely controllable reactions. In hydrogen production, which is equilibrium-limited and is dependent on the temperature at which the reaction proceeds, fine control of temperature is also important.

Key research directions to address these challenges include

- Improved microchannel combustion and reforming catalysts for long-term usability, including resistance to impurities
- Novel process reactor design (including novel reformers and shift reactors)
- Improved cooling systems/high-temperature materials for convective H_2 fired reformers
- Use of high temperatures for convective reforming in place of radiant (reduced steam production—lower energy loss)

Technology Impacts

The research will impact the CCUS scientific field by developing new understanding of process intensification technologies such as microchannel reactors and the wider application of complex cycles.

The general scientific community will benefit from new types of high-temperature materials for applications in other chemical processes and the availability of low-carbon H_2 (e.g., for production of ammonia, NH_3).

The principal impact of this work will be the wider availability of cheap, zero-carbon hydrogen for the net-zero emission energy economy. Allowing future energy systems to convert to hydrogen when its properties confer particular advantages over other zero-carbon vectors will improve the uptake of hydrogen from all sources (including renewable electrolysis).

- Hybrid processes for H_2 production offer opportunities to optimize performance, e.g., the use of heat from partial oxidation to complement reforming, provided that the challenges of achieving high heat fluxes can be overcome.
- Benefits can be expected through the integration of hydrogen production with power production by combining unit operations with heat integration.
- Economical hydrogen production from coal, heavy oil and other “difficult” fuels can be achieved provided these novel approaches are made resistant to the impurities and other issues that these fuels introduce.

Conclusions

This research on alternative lower-cost combustion-based technologies for H_2 production will help make CO_2-free hydrogen widely available for

- Industrial processes
- Heat
- Transport
- Ammonia production (fertilizer, energy vector)

It has many synergies with work proposed in high-intensity pressurized combustion, in particular the general interest in ion transfer membrane materials (although the applications have specific requirements). It will advance thin-film membranes for producing high-purity hydrogen for applications such as fuel cells and liquefaction for long-distance transport.

Hydrogen from fossil fuels is receiving renewed interest, given the interest in CCS, as a key tool for enabling net zero emissions rather than just as a simple oil replacement fuel (as in the 1980s to early 2000s).

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3. Carbon Dioxide Utilization

Increasing levels of CO_2 in Earth's atmosphere make CCUS one of the most urgent and important challenges faced by the global society. Although technologies for CCUS have advanced in recent years, today's technologies are still costly and energy-intensive, and significant advances are needed before more viable CCUS technologies are realized. In developing various carbon storage options, one particularly important need is the development of new processes to convert the captured CO_2 into useful commodity materials and chemicals, which are currently produced from fossil fuels, such as oil and natural gas. Effective means of producing commercial products—from liquid fuels to myriad materials used in consumer products (e.g., polymers)—could help drive the economics of CCUS processes and provide pathways to decarbonize sectors beyond power generation such as chemicals and materials sectors.

Nature converts CO_2 into materials via photosynthesis, ultimately producing biomass. Humans can convert CO_2 to fuels, chemicals, and even inorganic materials using engineered chemical and biological processes (Figure 3.1), if carbon-free energy (i.e., heat, electrons, and H_2) from renewable sources is readily available. Capturing and converting CO_2 from a wide range of emission sources—including energy generation sources, industrial sources, and even directly from the air—will enable new CO_2 utilization technologies with integrated storage options that will reduce CO_2 accumulation in the atmosphere. Further, such processes have the potential even to reverse this accumulation, perhaps making it possible to achieve the dramatic shift to negative emissions. Carbon dioxide upcycling as carbon-neutral or low-carbon materials also opens the door to the effective use and storage of locally available, intermittent renewable energy sources.

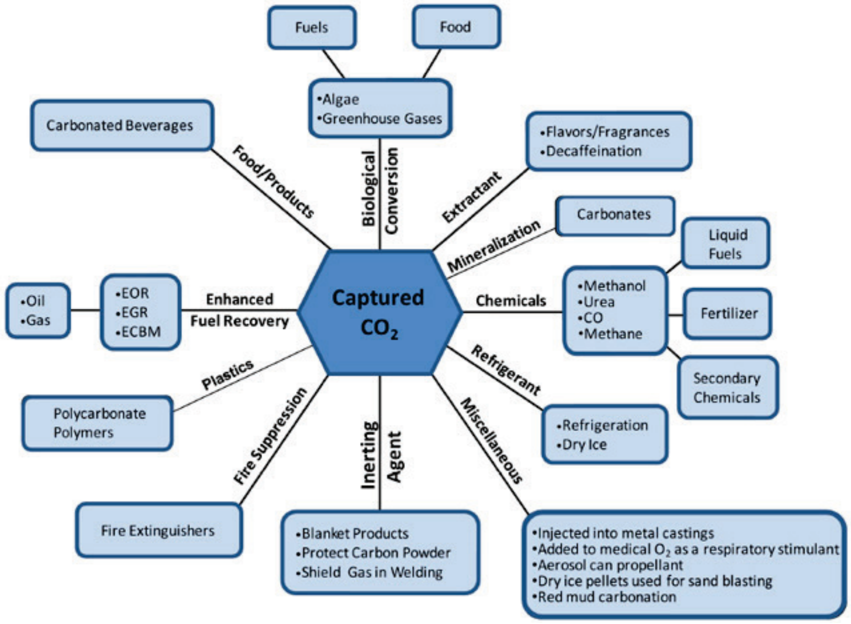


Figure 3.1. Schematic illustrating the uses of CO_2. The sizes of bubbles do not correspond to the size of the market or their carbon utilization and storage potentials. | Image courtesy of National Energy Technology Laboratory from CO_2 Utilization Focus Area

The vision for CO_2 utilization research is to advance science and develop innovative technologies that provide sustainable energy and materials while maintaining the stability of Earth's natural systems. To address this ambitious goal, four main pathways were selected for discussion at the Mission Innovation workshop. A fifth theme was added during the workshop based on active cross-panel discussions.

1. Thermochemical Conversion and Hydrogenation of CO_2
2. Electrochemical and Photochemical Conversion of CO_2
3. CO_2 Conversion to Solid Carbonates
4. Biological Conversion of CO_2
5. Enhanced Hydrocarbon Recovery with Carbon Storage

The development of novel energy and materials conversion pathways and technologies—particularly with reduced environmental footprints (i.e., net CO_2 emissions)—is a challenge that cannot be met by simply employing traditional scientific or engineering approaches. More than ever, the development and implementation of CCUS technologies require crosscutting collaborations among different disciplines. Important factors considered for the implementation of CO_2 utilization include (but are not limited to) capacity, economic feasibility, sustainability of reactants and energy sources, characterization and certification of new materials (e.g., construction materials) and permanence of carbon fixed in products.

The fundamental challenges raised in each of the five main CO_2 utilization areas involve

- Development of effective thermal and (photo)electrochemical catalytic reaction pathways via multiscale modeling and controlled synthesis
- Mechanistic and kinetic understanding of highly heterogeneous minerals and industrial waste systems for inorganic carbonate formation
- Use of CO_2 in enhanced recovery of unconventional hydrocarbons such as shale gas and oil
- Acceleration of biological CO_2 activation
- Innovative integration of sustainable reactants and energy
- Functionalization of new materials

The fundamental knowledge gained from this research will not only accelerate the development of CO_2 utilization technologies but also impact CO_2 capture and storage research and development, and ultimately, the economics of CCUS processes.

3.1 Utilization Panel Report: Thermochemical Conversion and Hydrogenation of CO_2

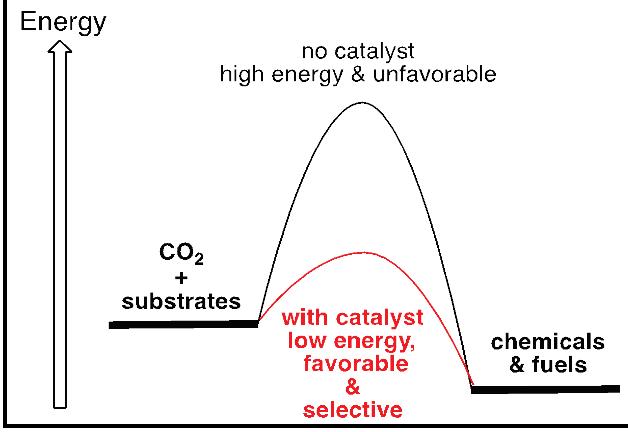
One of the main routes for CO_2 utilization, in terms of both volume of CO_2 used and potential economic benefit, is its thermochemical conversion and hydrogenation into fuels, chemicals, and materials. Thermochemical conversion uses heat and/or reactive chemicals to convert CO_2 into valuable new products. Carbon dioxide reduction is a chemical reaction in which the oxidation number of carbon decreases as it gains electrons, for example, by the formation of carbon–hydrogen (C–H) and carbon–carbon (C–C) bonds. In the case of CO_2 hydrogenation, H_2 is the chemical partner providing the electrons. The amount of energy required for the CO_2 transformation is determined by the extent of reduction.

Catalytic processes have been optimized over many decades by the chemical and chemical engineering communities to convert fossil fuels to commodity chemicals and materials. However, catalytic conversion of CO_2 to useful products provides unique challenges to catalytic processes because of the inherent stability of CO_2. In addition, for applications in CCUS processes, the catalysts are often challenged by potentially higher water levels and impurities such as SO_2 in the emissions that can severely reduce the lifetimes of the catalysts. Another important consideration is that catalytic conversion requires external energy input. Breakthrough catalytic transformations are needed to enable the valorization of CO_2 streams in a selective and energy-efficient manner to produce established and new products. Because a number of interesting CO_2 conversion technologies have poor equilibrium yields, highly active catalysts are needed to allow reactions to reach equilibrium as quickly as possible and, in combination with advanced reactors and other chemical process technologies, to access a greater range of CO_2-based products and materials (see the sidebar "Why is Catalysis Necessary").

Beyond chemicals and fuels, few available pathways can use CO_2 as a feedstock to produce key structural and/or functional carbon-based materials such as polymers, carbon fibers, and composites. Existing commercial production methods are very energy intensive and have a large emissions footprint and environmental impacts. The current production and market sizes as well as costs of these carbonaceous products are limited compared with the amounts of CO_2 emissions; thus, the deployments of products derived from captured CO_2 should be carefully designed so as not to quickly flood the market. The development of methodologies to produce these materials directly from CO_2 will reduce the overall emissions and environmental impacts of current processes while allowing for increased deployment.

The main fundamental challenges associated with CO_2 conversion to chemicals and fuels include the sustainability of co-reactants and catalysts. For example, to synthesize hydrocarbon materials, "magic hydrogen" that has a lower or zero carbon footprint is needed. Where will it come from? Also, the development of earth-abundant catalysts is highly desired.

Why is Catalysis Necessary?



Many reactions occur only if energy is supplied. The activation energy is the barrier that must be overcome to enable the reaction to take place; a catalyst is an agent that lowers the activation barrier. The use of a catalyst can lower the amount of energy needed, increase the rate at which the reaction takes place, and increase the yield while decreasing the costs.

The industrial world relies on catalysts; fuels, pharmaceuticals, fertilizers, plastics, foodstuffs, and fabrics are examples of items manufactured by use of catalytic processes. In fact, over 85% of chemical processes involve catalysis. Therefore, finding new, improved catalytic routes is always desirable.

3.1.1 Status of Thermochemical Conversion and Hydrogenation

Carbon dioxide is a chemically stable compound. Energy must be supplied to change or break carbon–oxygen bonds to transform CO_2 into more valuable products. The transformation can be accomplished in several ways – using heat, pressure, a high-energy reactant, electromagnetic radiation, or a combination of these. In many cases, particularly transformations that require breaking a C=O double bond, hydrogen is needed, as it is a high-energy reactant. (Note that production of hydrogen for those processes from renewable sources rather than fossil sources to enable true low-carbon approaches would be highly desirable.) As an alternative, simply changing a C=O double bond to a C–O single bond will allow the incorporation of CO_2 into organic, inorganic, or polymeric carbonates, carbamates, and ureas without requiring significant chemical reduction and the associated energy inputs.

To reduce the overall energy requirement of the reaction, a catalyst can be employed. Catalysts are used in the majority of thermochemical and hydrogenation reactions of CO_2. For example, in Figure 3.2, the synthesis of methanol requires heat, a catalyst, and a higher-energy co-reactant, hydrogen. Carbon dioxide reacts with three molecules of hydrogen over a catalyst under high temperature and pressure to produce methanol. An added complication, though, is that the reaction is in equilibrium, so the products must be removed. And as is common for many reactions, the removal of water is essential.

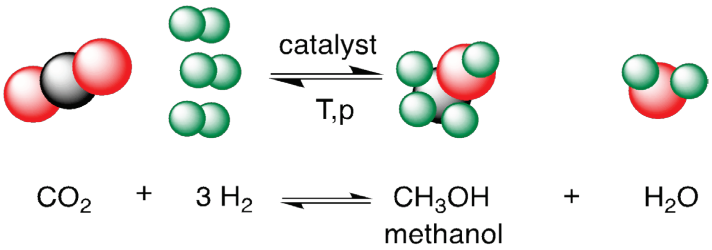


Figure 3.2. Thermochemical conversion of CO_2 to methanol. | Image courtesy of CO2ChemNetwork. Reproduced with permission.

Many CO_2 transformations and reductions use catalytic systems containing an array of different metal catalysts to maximize conversion efficiency. In many cases, the sustainability of the metal used as the catalyst is not considered. Common catalysts employed include noble and precious metals, such as ruthenium, rhodium, and palladium; and development of lower-cost and more sustainable catalysts is a high priority. Figure 3.3 shows the availability of catalytic materials.. Catalyst choice is often a compromise between high chemical and thermal stability and selectivity and activity. High selectivity may be achieved by designing sometimes elaborate organic ligands to surround the metal active site. However, such organic ligands are often thermally unstable at temperatures exceeding 130°C. The use of micro- and meso- reactor technologies can be beneficial, as their unique properties can result in large increases in reaction rates, allowing higher temperatures and more sophisticated catalysts to be employed.

Organocatalysts offer advantages over metal catalysts in that they are often low in cost, nontoxic, and more sustainable. Reported organocatalysts for CO_2 reactions include nitrogen-based heterocycles, organic and molten salts, ionic liquids, and (poly)phenolic and poly-alcohol compounds. Currently, these catalysts cover a small range of coupling reactions, including the production of methane, methanol, cyclic carbonates, and diones and formyl compounds. Organocatalysts are generally less efficient and require more energy input than metal-based catalysts. This penalty is usually overcome in the form of higher catalyst quantities, higher temperatures, and longer reaction times. In addition, organocatalysts enable simpler separations and generally have good water stability.

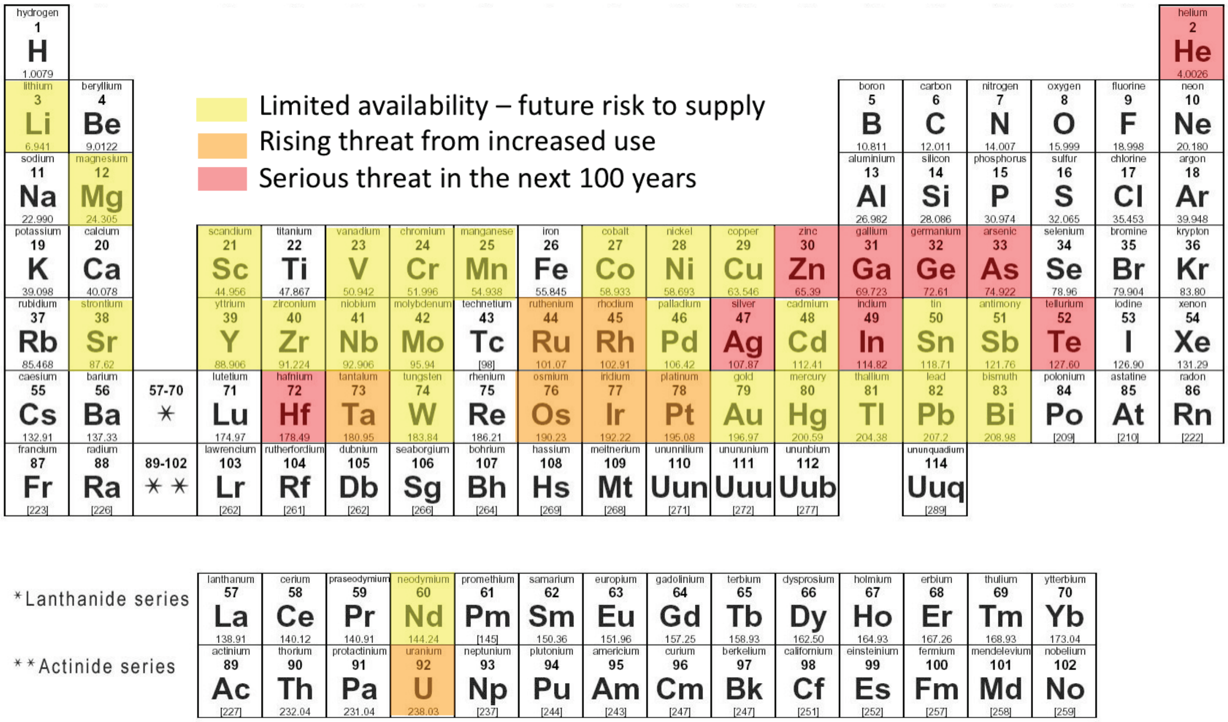


Figure 3.3. Sustainability of elements. | Adapted by Ah-Hyung Park from the web page Endanged Elements

Carbon dioxide reacts with a range of organic compounds, such as alcohols and amines, to produce useful chemicals for the pharmaceutical and agrochemical sectors, including open and cyclic carbonates, ureas, and carbamates. In this case, the C=O double bond is reduced to a C–O (or C–N) single bond, which requires much less energy than complete C=O double bond conversion to hydrocarbons. This can be illustrated by the reaction of CO_2 with epoxides to yield cyclic carbonates. Although CO_2 reacts with epoxides to form cyclic carbonates—a reaction that exploits the ring strain energy of the epoxide—the type of cyclic carbonate that results depends completely on the limited range of available epoxides. A much more general route to cyclic carbonates would be via a simple alcohol or diol. The problem with these reactions is that the equilibrium yield is limited to only a few percent of the desired product, with water as the by-product. This challenge has thus far been addressed by the chemical absorption of water by co-reagents such as organic nitriles [Honda 2014]. However, the resulting products from the reaction with water are neither readily recyclable nor useful, and the need for such a co-reagent increases the cost, energy footprint, and complexity of the reaction, rendering it industrially irrelevant.

Carbon dioxide reduction may occur in several stages to remove oxygen in a stepwise manner. The removal of one oxygen, the least energy-intensive stage, yields oxygenated products such as methanol and carbon monoxide, which can then be converted to a variety of chemicals and fuels. Further reduction reactions can remove the second oxygen to yield hydrocarbons [France et al. 2014; Jiang et al. 2010]. Currently, there is only coarse control over hydrocarbon chain length distribution and selectivity in these reactions; good control is important to allow the creation of synthetic gasoline and diesel. High-temperature catalysts such as iron yield short-chain products, whereas high-temperature catalysts such as cobalt yield long-chain products [Maitlis and de Klerk 2013]. Highly desirable targets are kerosene (C12) and diesel (C18), as these are direct drop-in fuels for high-energy-density, long-haul transport applications. Thus, short hydrocarbons need to undergo further chain extension or longer products need to be hydrocracked (requiring more hydrogen) to produce chain length distributions around the desired product sizes. There are no examples in which control over selectivity is inherent. Selectivity is important if fuels are to be produced at competitive prices and at specifications acceptable to the aerospace industry, in particular.

Of the many diverse sources of CO_2, all vary in composition and purity; even single streams can vary from day to day depending on process inputs and external conditions. Flue gases from power generation, for example, are typically 10–12% CO_2 by volume, the remainder being nitrogen with impurities such as oxygen, acid gases, and, critically, water. Often CO_2 reactions are based around pure CO_2 sources, necessitating capture and purification technologies that increase process costs. If waste gases containing CO_2 can be used in reactions directly, then significant savings can be realized. If reactions are carried out under pressure, the initial compression stage can be used to condense out water that could inhibit the reaction. In some cases, CO_2 can be used directly from flue gas or, more typically, from simulated flue gas. Impurities in the mixed gas streams often pose problems, poisoning the catalysts or simply reducing the reaction kinetics. Hence, more robust catalysts are required for conversion of mixed gas streams.

Although the chemical industry is driven by catalytic reactions, the use of stoichiometric reagents that are cycled (looped) in the synthesis is also important. One example is the use of Grignard reagents (RMgX) formed from organic halides and magnesium. The halide can be produced from methanol, which in turn can be prepared from CO_2. The Grignard reagent reacts with the organic halide, which after acid quenching yields carboxylic acid (RCO_2H) and magnesium halide (MgX_2). The latter can be electrolyzed in a standard industrial process to regenerate magnesium metal, which is a source of higher energy relative to CO_2, and the dihalogen (X_2), which can be used to produce more Grignard reagent and organic halide from methanol (Figure 3.4) [Dowson and Styring 2017]. Although not catalytic, the active metal is recovered and regenerated in a separate reaction cycle. Analogies can be drawn with the interconversion of NAD^+ and NADH in biological systems. This approach may prove valuable in the chemical industries because it allows processes to be carried out under milder conditions (as the metal co-reactant is energy rich). In addition, because the metal is present in stoichiometric amounts, it is easier to separate from the products, even in a continuous flow process. Using commercially available reprocessing techniques will also benefit the cost of production.

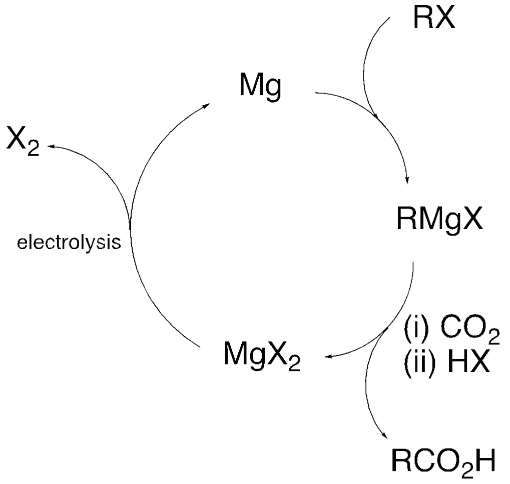


Figure 3.4. Chemical looping reaction using magnesium. | Reproduced from G.R.M. Dowson and P. Styring. 2017. *Energy Res.* **12**, Demonstration of CO_2 conversion to synthetic transport fuel at flue gas concentrations. Courtesy of Peter Styring

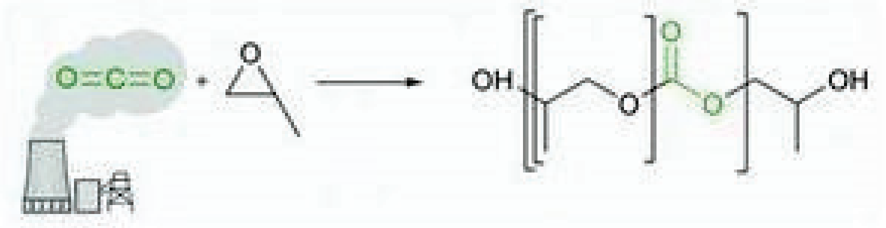
Plasma (ionized gas) generation is a potentially promising approach for the realization of chemical conversion of CO_2 using renewable energy. From a practical point of view, plasma is advantageous in this context because it can be rapidly switched on and off. This makes it suitable for matching chemical production to variable and intermittent power generation. Technologies for plasma generation are well established and capable of being scaled to industrial levels. One of the major attractions of the application of plasma for CO_2 utilization is the potential for efficient coupling of electrical energy directly into chemical transformations. Energy efficiencies approaching 90% for dissociation to CO have been reported in the case of microwave-generated plasma [Fridman 2008]. However, there is a lack of fundamental understanding of how plasma can best be used to drive chemical conversion in a selective manner. Plasma activates molecules by storing energy in the form of internal degrees of freedom. Depending on the electron temperature, the plasma electrons may transfer most of their energy to a molecule's vibrational modes, which is thought to be an effective means of reducing activation barriers to chemical reaction of CO_2. Although there have been phenomenological studies of the application of plasma to drive CO_2 conversion, both in pure and mixed gas phases, fundamental understanding of coupling among the different modes of molecular excitation, and how it can be optimized to maximize conversion and energy efficiencies, is still lacking. Novel strategies for the removal of oxygen from the product stream are also required.

Looking beyond chemicals and fuels, production of polymers and other functional materials is limited to a few key reactions to produce polyurethane polyols, polycarbonates, and carbon nanofibers. Thus far, the most successful application has been achieved without significant change in the oxidation number of carbon by inserting CO_2 molecules into the polymer chain while retaining both oxygen atoms. Specifically, a “dream reaction” was developed to use CO_2 as a co-monomer, together with epoxides, in the synthesis of oligomeric (short-chain) poly(carbonate)ols that are later used in polyurethane synthesis (see the sidebar “Creating New Dream Reactions”). The new pathway removes the need to use phosgene, a harmful gas, in the synthesis and reduces the overall carbon footprint by 9–20% [von der Assen and Bardow 2014]. Polycarbonates, in which CO_2 serves as a co-monomer, can incorporate 50% of the gas by weight in polyethylene carbonate and 33% in polypropylene carbonate. One issue with these polymers is that they are inherently soft, so their range of application as pure polymers is limited and blending with other (petrochemical-derived) polymers is required to obtain robust, commercially applicable materials. Polyols in the “Converge” line demonstrate a 40% reduction in the heat of combustion compared with traditional polyols, making them more efficient fire-retardant materials [Converge 2017]. Carbon dioxide can be polymerized with dienes and alkynes, but the usefulness of these polymers is not known.

Creating New Dream Reactions

Imagine being able to take waste CO_2 and create solid, usable products that people want to buy. This dream has become a reality for the creation of the first plastic products from CO_2. After years of research for the optimal catalysts to enable the reaction to occur, the first polymers made from CO_2 are now beginning to launch into the market.

These CO_2-derived polymers are identical in chemical composition but often superior in properties to traditional polymers; for example, they offer improved adhesive and tensile strength, improved mechanical strength, and reduced heat of combustion vs. conventional polyols. The polymers have up to 40% lower greenhouse gas impact and can contain up to 50% CO_2 by mass.



A nascent area of materials synthesis is aimed at producing carbon-based functional and structural materials, including carbon fibers. The reactions are limited to carbon nanofibers at present, but there is a drive to develop continuous carbon fibers. It is reported that CO_2 can be extracted from the atmosphere and converted into carbon nanotubes for potential use as structural agents in composites [Wu et al. 2016]. Although nanotubes may have applications in electronic devices because of their high conductivity, it is unlikely that at the nanoscale they can impart true structural enhancement. The technology does not yet exist to produce continuous carbon fibers from CO_2, but these fibers have enormous potential due to their increasing use in composite materials for aviation and automotive construction [Frank et al. 2014]. As industries continue to look for new, lighter, more sustainable materials with which to construct less-energy-consuming vehicles and planes, CO_2-based materials offer the potential to create structurally robust materials that meet these requirements while using CO_2 outputs of various industrial and biological streams.

3.1.2 Scientific Challenges

Fossil fuels supply 85% of the world's energy needs and represent the largest source of anthropogenic CO_2 emissions. Petrochemicals currently supply over 95% of industrial, organic chemicals, such as plastics, insecticides, drugs, and fertilizers. In contrast, CO_2 is overlooked as a carbon source because it is a very stable compound, so that less than 300 Mt CO_2 per year are currently being transformed. Using CO_2 as a new carbon source hence represents a new perspective in the production of chemicals, fuels, and materials but also presents major scientific challenges:

- How can the entrance of new petrochemicals into the supply chain be avoided and CO_2 be transformed into both established and new products that have never been made from CO_2?
- How can functional and advanced materials be designed from CO_2?
- How can CO_2 streams of varying composition be used, including those with dilute CO_2 concentrations, high water levels, and additional impurities that may act as catalyst poisons?

Innovative synthetic routes must be designed to convert CO_2 and its chemical partners to useful products, using tools such as catalytic reactions, stoichiometric transformations, or chemical looping processes. There are opportunities to develop processes that avoid the use of toxic or environmentally questionable reagents. The overarching objective is to unveil new reaction pathways for the selective formation of C–H, C–C, and carbon–heteroatom bonds. This effort could include, for example, the discovery of solid, nanostructured, molecular, and/or multistage catalysts that enable the formation of compounds currently unavailable from CO_2, including olefins, heavier alkanes, and aromatics. Molecular understanding of the chemical steps involved in the activation of CO_2, the formation of new bonds, and the catalytic mechanisms is invaluable in guiding the synthetic efforts. Advanced computational and in situ characterization techniques represent important tools in this direction.

Energy efficiency is the first criterion in CO_2 conversion to fuels and chemicals, as the reduction of CO_2 is, by nature, energy intensive. Thus, suitable reductants, such as hydrogen, must be used to yield reduced products: formic acid, carbon monoxide, methanol, methane, or alkanes. A parallel challenge must thus be addressed: production of hydrogen and/or co-reactants at reasonable costs and from non–fossil fuel sources. Energy-efficient and intensified processes must be discovered to achieve the desired low life-cycle impact and cost-effectiveness to enable widespread CO_2 conversion.

Carbon dioxide utilization reactions are unlikely to yield single products. Even in atom-efficient reactions, such as cyclic carbonate formation, the formation of isomers, and hence a mixture, is a possibility. In most reduction reactions, water is produced and must be removed. Carbon dioxide hydrogenation may be limited by thermodynamic parameters, and as a result, not all reactants will be transformed into the desired chemical. One way to overcome these limitations is by removing by-products to drive the reaction beyond chemical equilibrium. By-products can be removed by a sorbent, a selective membrane, or by simple condensation. Intensification may be facilitated, for instance, through spatial and temporal control of reaction conditions or through separation techniques. New strategies for intensified catalysis and process engineering at fundamental levels to limit by-product formation would be advantageous.

One specific example of by-product separation is the production of dimethyl ether, which can be used as a diesel replacement, from CO_2 and hydrogen [Catizzone et al. 2017]. Under standard conditions, the conversion rate is limited to less than 10%. However, when a steam sorbent is added, the conversion rate is increased to greater than 60%. After some time, the sorbent becomes saturated and needs to be regenerated. The overall effect is an increased single-pass conversion, less demand on the downstream separating technologies, and smaller recycle streams. This approach requires new or improved high-capacity sorbents that can be easily regenerated and catalysts that can operate under transient conditions. Designing new combinations of catalysts and processes that permit in situ removal of low concentrations of water and other by-products directly during the reaction would increase the range of viable reactions and accessible products, providing more versatility for the use of CO_2.

In the case of traditional fuels, a key challenge is the selective synthesis of specific hydrocarbon chain lengths. Although wide molecular weight distributions are possible, narrow distillate fractions are preferable. Achieving narrow fractions will allow direct use without expensive fractionation and hydrocracking. The challenge is to produce catalysts that have sufficient activity to facilitate both C–C and C–H bond forming reactions yet are able to control chain growth. It is unlikely that specific catalyst design will be able to meet this challenge. Rather, the environment in which the catalyst operates will provide the control, perhaps by using solvents that control growth through specific solubilities at certain temperatures, or through a thorough understanding of reaction kinetics. This situation naturally leads to the use of dynamic continuous flow processing with built-in detection and feedback. For fuels, this method may be relatively simple through online gas chromatography with direct feedback. With sufficient knowledge about the reaction kinetics, time-dependent samples can be taken and the flow diverted to a noncatalytic section of the reactor where the product is collected. Further enhancement of the process may be possible through the synthesis of morphologically controlled catalyst supports with well-defined pore sizes. It may be achieved by templated synthesis. A novel development in recent years includes 3D printing of complex, porous geometries in metals, ceramics, polymers, and composites, allowing the structures of the catalyst monoliths to be tailored to the specific dimensions of a reactor.

More efficient catalysts are always desirable. Most industrial processes involve heterogeneous catalysts with the catalyst in a different phase (usually solid) from the reactant mixture (which may be a liquid, solution, or gas). Heterogeneous catalysts allow easy processing, as they can be readily recovered from the reactor and recycled. This ease of processing comes with the compromise that the activity may be reduced, and there is little opportunity to control selectivity. By contrast, homogeneous catalysts are in the same, usually solution, phase as the reactants. The advantage is that high activity and selectivity can be achieved, but it comes at the expense of durability, ease of separation, and recycling. As many homogeneous catalysts are based on metal–ligand systems, thermal stability is limited to prevent decomposition of the organic ligands. It is therefore desirable to investigate the possibility of combining homogeneous catalysts with heterogeneous supports to produce hybrid systems that combine the activity and selectivity of homogeneous systems with the ease of separation, recyclability, and thermal stability of heterogeneous systems.

The development of organocatalysts is a small, emerging field with a number of advantages based on the sustainability, low cost, and low toxicity of the catalysts. Much still must be understood about the mechanisms involved, and only a small number of reactions have currently been observed. For example, although five-member cyclic carbonates have been achieved by organocatalysis, the formation of six-member cyclic heterocycles is still at a fundamental stage of research. Carbon dioxide and epoxides readily produce either five-member cyclic carbonates or polycarbonates. The cyclic carbonates are the thermodynamic product, and the polymers are the kinetic product. However, in a six-member ring, the six-member cyclic carbonates are thermodynamically under ring-opening polymerization, as the polymer is the thermodynamically favored product. Furthermore, oxetanes (the four-member ring equivalents of epoxides) are not very readily available. A challenge would be to start with a 1,3-diol, such as 1,3-propanediol, and polymerize it with CO_2. However, the thermodynamic issues with equilibria and water formation will remain.

Decreasing the required energy inputs for organocatalysis by lowering reaction temperatures and pressures is a key challenge, along with increasing selectivity and yields. New approaches and methodologies are needed that use cooperative confinement and/or site-isolation effects to produce the next generation of highly effective, sustainable catalysts. In addition, catalysts are needed that are insensitive to water. Further, it may be possible to design reactors and processes that permit efficient removal of low concentrations of water at relatively high temperatures. All of these approaches provide an intriguing entry to producing many commercially important products from CO_2.

Another route for CO_2 conversion is using energy from plasmas or microwaves, which can become economically viable with increasing availability of renewable energy sources. Further, plasma catalysis, in which plasma-activation is coupled with a catalytic material, can be used to enhance conversion and selectivity for more complex transformations of CO_2 (e.g., hydrogenation, C–C coupling). This combination typically allows for reductions in catalyst loading and/or reactor operating temperature compared with a purely catalytic system. In addition, the pre-activation of CO_2 by plasma can relax demands on the catalyst and may allow for material substitution that reduces or eliminates the requirement for scarce elements. To fully realize the benefits of plasma catalysis, better understanding of the fundamentals of surface interaction involving pre-activated molecules is required. This involves determining the most effective modes of excitation for promoting reactions at surfaces and the best catalyst compositions and structures for the use of these modes. This understanding will facilitate the development of catalytic systems, from atomic to macroscopic scales, that are specifically designed and tailored to complement the plasma phase.

Because plasma activation is an effective means of promoting bond dissociation, it may also offer a viable route to the complete reduction of CO_2 to carbon, facilitating the production of carbon-based materials. Major issues to overcome in this approach would be the need to (1) manage the oxygen inventory released to avoid back-reaction and low efficiency in carbon production and (2) control the composition and morphologies of the carbon produced to maximize its value for the production of high value functional materials.

A major challenge in CO_2 catalysis is feedstock purity. One of the major barriers to CO_2 use is the cost of pure CO_2. However, if suitable catalysts can be developed that are more robust toward activities and active toward low concentration streams, then there is no reason why waste gas supplies cannot be used. The major component of waste gas mixtures will be dinitrogen and methane for flue and biogases, respectively, and more complex mixtures for off-gases from the iron and steel industries. Apart from its dilution effects, which will affect reaction kinetics, N_2 is not a problem. Indeed, at flue gas concentrations, CO_2 is present as a 3 M gaseous mixture, while most reactants in solution are typically 1 M or less. In many catalytic reactions, N_2 is used as an inert gas to help preserve catalyst activity. Therefore, detailed kinetic studies are needed to determine the trade-off between reduced-rate-form CO_2 dilution and the reduced costs of eliminating a separate carbon capture and purification step. Direct CO_2 adsorption and conversion in a single step, or a multiple-step, multiple-site single catalytic reaction should therefore be considered a major priority.

Although there is substantial literature on the synthesis of straight-chain hydrocarbons, carbonates, and cyclic carbonates, significantly less research has been performed on the synthesis of alkenes and aromatics. Alkenes (olefins) are regarded as the building blocks of the chemicals industry, so direct conversion of CO_2 to ethene (ethylene) and propene (propylene), in particular, is considered highly desirable. The direct conversion of ethene with CO_2 to yield acrylic acid is also desirable, as it opens up sustainable routes to the production of acrylic acid and, subsequently, poly(acrylic acid), a major commodity chemical. Catalysts that would promote the efficient insertion of CO_2 into C–H bonds would provide a route for the direct formation of organic carboxylic acids.

Similarly, aromatics and heteroaromatics are key components of many commercial products, including pharmaceuticals, commodity chemicals, and materials. At present, the conversion of CO_2 to aromatics proceeds through the alkene, so they are therefore intimately linked. In a typical process, CO_2 is converted to methanol, which is then self-condensed to give dimethyl ether, which is used to produce ethene on subsequent dehydration. Cyclization of the alkenes then leads to aromatics. Direct conversion would therefore save time and money.

CO_2 conversion also has huge potential for the production of highly desirable commodity chemicals. Controlling and enhancing the properties of a material by incorporating CO_2 can originate new and advanced materials in the form of polymers, composites, nanocarbons, and carbon fibers. This will allow for the tailoring of materials properties, potentially opening them up for an even wider range of applications. Strategies must be developed for the use of CO_2 as a co-monomer in the synthesis of polymers with controlled molecular weights and distributions. Approaches for the directed synthesis of materials with controlled nano- and micro-structures from CO_2 should be explored, particularly routes that avoid toxic and polluting reagents and/or high-energy processes, as currently implemented in existing production methods.

Another class of carbon-based materials are composites based on carbon fibers. These materials are increasingly being used to displace the weight while maintaining the strength of conventional structural materials—such as steels and aluminum—in automobiles, airplanes, and other applications. Carbon fibers are currently made from polyacrylonitrile (PAN), which is drawn into fibers possessing molecular alignment in the direction of the developing fiber. The fiber is then cross-linked to give fibers whose alignment is locked in. Subsequent anaerobic decomposition of these polymer fibers results in carbon fibers with high directional strength. These can then be woven into larger fibers or mats and mixed with polymers to produce high-strength, lightweight fibers. The challenge is to produce low-cost polymers derived from CO_2 that can be used to replace PAN, which is both expensive and toxic. These new polymer precursors must be capable of self-assembling into structurally aligned fibers, and processes must be developed to rapidly remove the oxygen from the thermal decomposition of the polymers to prevent the reoxidation of carbon. Branched poly(carbonate)s may provide a suitable and sustainable route to such polymers. The market for carbon fiber is rapidly growing in the aerospace, automotive, and construction industries. However, supply will not be able to match demand, and less-polluting processes are urgently needed.

The range of co-monomers that can be polymerized with CO_2 needs to be increased. If the issues of low equilibrium product yields from the reaction of CO_2 and alcohols or amines could be addressed, then biomass-derived diols or diamines could be exploited to make polycarbonate or polyurea materials not currently accessible. Aromatic polycarbonates (as opposed to the aliphatic polycarbonates derived from CO_2 and epoxides) are thermoplastic polymers with a range of applications. They cannot yet be made from CO_2, but they could be feasible if efficient reactions for the synthesis of cyclic carbonates from CO_2 and alcohols could be developed. Carbon dioxide and alkenes can be coupled to make acrylic acid derivatives that can eventually be polymerized. Better catalysts and processes are needed. Larger-scale polymers, such as formaldehyde-based polymers, can be developed if CO_2 can be efficiently reduced with two equivalents of H_2 to produce formaldehyde.

3.1.3 Why Now?

Effective utilization of CO_2 produced from the combustion of fossil-derived fuels is a critical component of any CCUS strategy. Production of high-value chemicals and materials from CO_2 is a grand challenge that can be met with the discovery and development of a new generation of highly efficient and selective chemical processes. Further, today the chemical industry is highly dependent on fossil-based feedstocks, and nearly all organic chemicals are derived from fossil fuels. Carbon dioxide released in combustion and industrial waste streams represents an nearly untapped source of carbon to produce highly valuable chemicals and materials that can displace fossil fuels and drive the economic case for CCUS. Although CO_2 is an abundant source of carbon, its value has not been realized because it is highly stable, oxygen-rich, and found mainly in impure streams. These factors create challenges in converting CO_2 to value-added compounds. Current catalytic technologies, optimized to convert oxygen-poor feedstocks to produce fuels and chemicals, cannot be translated to CO_2 conversion. Therefore, there are insufficient methodologies for CO_2 conversion. Breakthrough catalytic transformations will enable the selective, energy-efficient valorization of CO_2 streams to established and new products. Recent advances in reactor design, process intensification, characterization methods, and separation techniques are enabling the elucidation of new catalytic systems, making now the right time to open up this new source of carbon and contribute to the circular economy.

Production of lighter-weight, stronger, advanced materials—such as carbon fibers, polymers, and composites—for automobiles, trucks, and airplanes can reduce the energy needed to travel the same distance. Markets for advanced materials are rapidly increasing but are limited by material production routes. Opening new, green, sustainable pathways using CO_2 could enable a rapid expansion of the sector, which would not only reduce emissions from processing but also avoid emissions by reducing vehicle fuel requirements.

The rapid expansion and decrease in the prices of renewable energy have opened processing routes that were previously not economically viable. Deploying new catalytic technologies involving plasma or microwave energy is a radical new approach. The first advances in these approaches have indicated new, efficient, flexible transformations of CO_2, but much fundamental work remains to be undertaken, specifically regarding the use of real flue gases, design, and scale-up. These processes could efficiently use increasingly abundant renewable energy, enabling effective energy storage solutions using chemicals and synthetic fuels to balance seasonality issues.

3.1.4 Conclusion

The discovery of new, efficient, and selective processes for conversion of CO_2 to useful chemicals and materials is a critical component of CCUS strategies. Researchers need to think outside the normal constraints of synthesis, seeking new routes to commodity chemicals and materials, and even new products. New ways of activating CO_2 using catalytic processes, novel energy sources (such as plasmas) or even combined processes are key to unlocking the potential of using what is currently a waste product to make economically useful products.

3.2 Utilization Panel Report: Electrochemical and Photochemical Conversion of CO_2

The vision for success is the development of new processes that balance global CO_2 emissions from anthropogenic activities with global CO_2 utilization and uptake, resulting in net zero or perhaps even negative emissions. An important part of reaching that goal is the development of means to utilize waste CO_2 emissions as a feedstock for carbon needs that would normally be met by fossil fuels. The challenge is to supplant nonrenewable resources—now the main source of carbon atoms in fuels, plastics, lubricants, and fine chemicals—by using the numerous available point sources of CO_2 and doing so in a completely renewable manner (Figure 3.5). In the longer term, deriving CO_2 directly from the atmosphere may be possible.

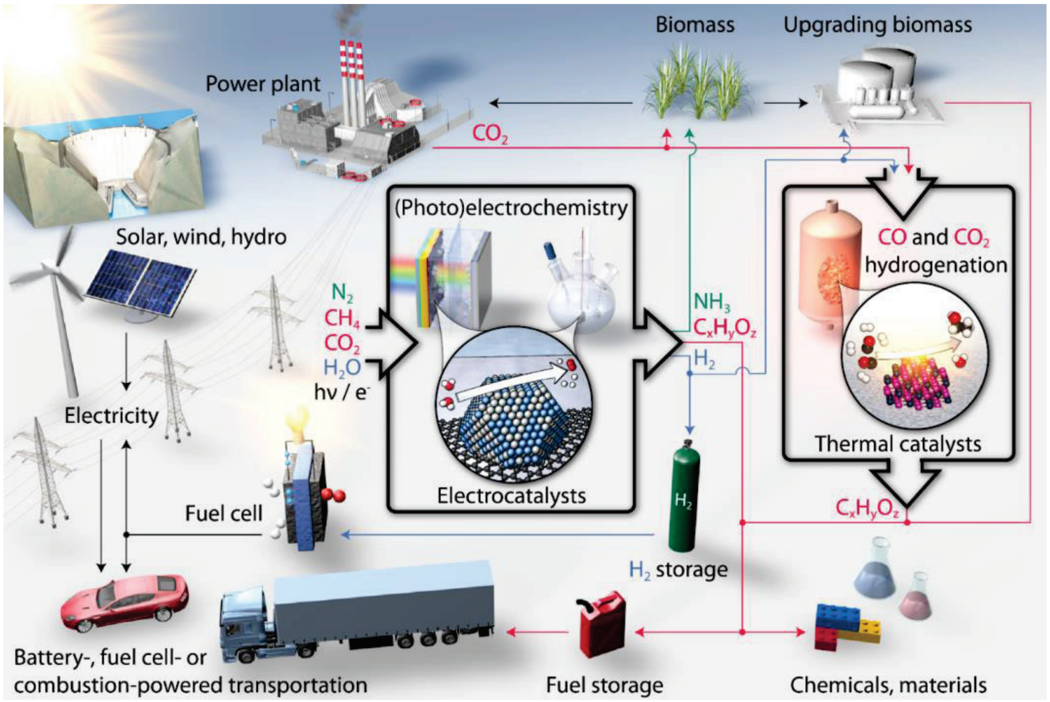


Figure 3.5. A vision for the future: sustainable production of fuels and chemicals, using carbon-free energy (e.g., wind, solar, hydro, etc.) and sustainable feedstocks. New processes must be developed, and significant R&D investment will accelerate, materializing a sustainable future. | Figure adapted from Seh et al. 2017. *Science* **355**(6321), eaad4998

Because CO_2 is in a stable and low-energy state, the conversion of CO_2 into any other product requires the input of energy. Nature drives this process naturally in the form of photosynthesis through an energy input of solar photons. Artificial photoelectric and photosynthetic systems have been developed, such as photovoltaic panels, but the development of a direct substitute for photosynthesis is so far unrealized and must be developed. Scientific efforts to date provide the foundational knowledge upon which further R&D efforts can be built to develop sustainable processes that use CO_2 in productive new ways. Photochemical CO_2 conversion holds the promise of broad-scale capture of energy from the sun in a storable liquid form. Electrochemical CO_2 conversion offers flexibility for capturing and storing energy from all renewable sources, such as wind turbines, photovoltaic panels, and others.

The time is right to embark on these tasks; substantial scientific progress has been made in recent years toward the necessary electro- and photocatalyst systems, and the cost of renewable electricity has dropped significantly, with continuing price drops allowing markets to open up toward renewables at an unprecedented rate. This change in the economics of renewable electricity means that a substantial opportunity is emerging in many markets where, during periods of peak generation, optimal wind or insolation will result in electricity available at a marginal price of nearly zero. Broad deployment of electrochemical CO_2 conversion will create an opportunity to store excess energy and to balance an electrical grid powered by variable, renewable electrical energy sources. At present, there is no cost-effective means to store large amounts of excess electricity, and the variable nature of wind and solar creates a need for spinning reserves that are typically fossil fuel powered. This non-ideal situation could potentially be mitigated by having rapidly dispatchable commercial electrochemical processes that could be quickly idled or throttled in response to variability in renewable generation.

This report outlines the scientific needs and challenges that must be overcome to enable this vision of the future, the electrochemical and photochemical conversion of CO_2 to fuels and chemicals (Figure 3.6). The challenges include the development of exquisitely controlled catalysts and catalytic systems. This will necessitate advancements in materials science, molecular chemistry, single-atoms characterization, and in situ/operando measurement, among many other areas in science and engineering.

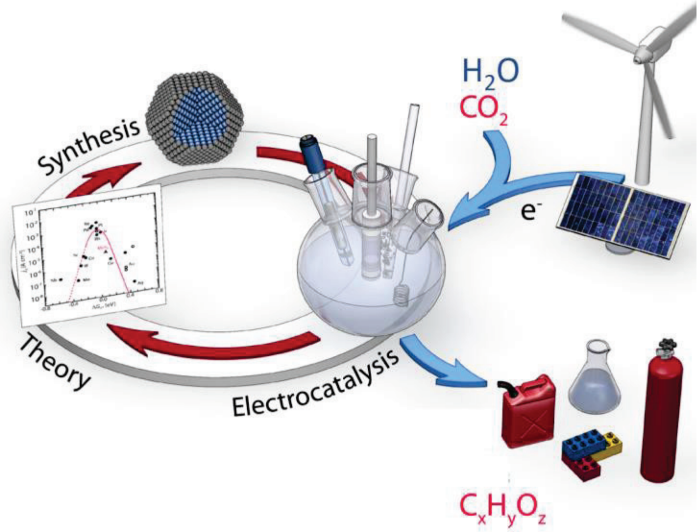


Figure 3.6. Support of R&D efforts can enable new processes that utilize renewable forms of electricity to convert CO_2 into desirable carbon-based products, including fuels, materials, and chemicals. One of the keys in developing such processes is combining theory, computation, and experimental studies to provide the insights needed to overcome technical barriers. | Figure adapted from Seh et al. 2017. *Science* **355**(6321), eaad4998

3.2.1 Status of Electrochemical and Photochemical Conversion

The simplest form of CO_2 electrolysis is the conversion of CO_2 to CO, which is an important intermediate for chemical syntheses. Solid-oxide electrolyzers (kilowatt scale) that convert CO_2 into CO at greater than 90% electrical efficiency are now commercially available (see the sidebar "Commercial CO_2 Electrolyzers"). Ambient temperature electrolyzers (100 W scale) that convert CO_2 to CO or formic acid are also in commercial development (Figure 3.7). Although ambient-temperature electrolyzers exhibit less than optimal efficiencies, mainly owing to limitations of the anodes, they can be combined with water electrolysis to produce synthesis gas (syngas). Syngas can be converted into many of the fuels, chemicals, and plastics used today through processes developed and optimized over the last 100 years. While these are excellent demonstrations of the scale-up of CO_2 conversion to CO, much remains to be learned regarding operation and durability under a wide variety of conditions such as variable power and impure streams of CO_2. A short-to-medium term opportunity is to combine CO_2 electrolyzers with biochemical systems to create products that cannot be manufactured by conventional catalytic methods. CO_2 and water electrolyzers have been combined with bioreactors to produce electrofuels, alcohols, organic acids, and edible biomass such as animal feed. These hybrid processes have been shown to be highly selective for final products, but the energy efficiency is modest and significant post-processing is required to concentrate dilute product streams.

Commercial CO_2 Electrolyzers Have Begun to Arrive

Think it's a pipe dream to use renewable electricity to convert CO_2 into carbon-based fuels and chemicals? Not at all! Commercial CO_2 electrolyzers are beginning to enter the market at the kilowatt scale, using electricity to convert CO_2 and H_2O into CO. These advances inspire many future R&D efforts.

Image courtesy of Haldor Topsøe A/S

The electrolyzer shown (Haldor Topsøe) can produce 2 m^3/h of pure CO with nearly 100% energy efficiency. Much R&D is needed to build from this work—for instance, electrolyzers that can

- produce other valuable products (e.g., methanol, ethanol, ethylene)
- operate with variable electricity sources, and with different input sources of CO_2
- scale up to the megawatt and gigawatt scales

This report and the associated PRDs identify the research pathways needed to enable such technological advances for sustainable chemical processes at impactful scales.

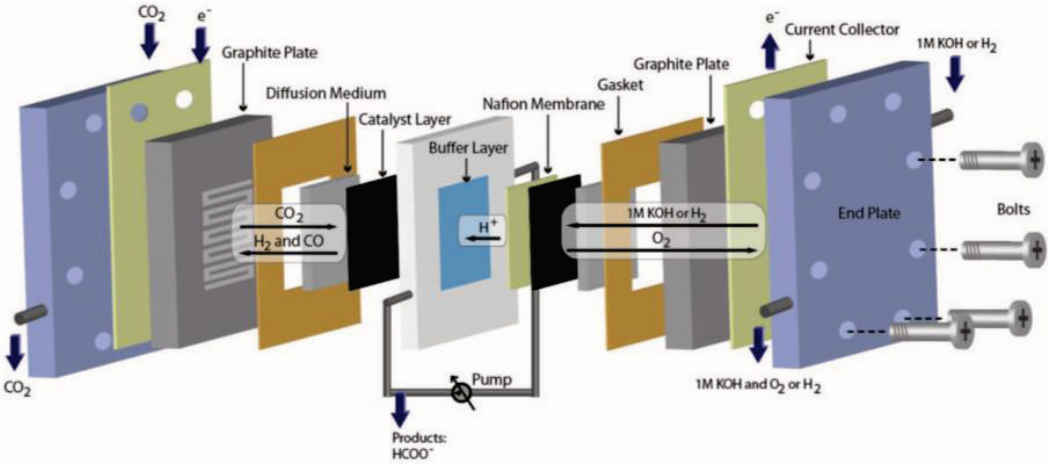


Figure 3.7. Exciting opportunities are ahead in CO electrolysis. Commercial CO_2 electrolyzers that produce CO have recently entered the market at kilowatt scale (see the sidebar). Demonstrations of lab-scale electrolyzers have shown that other desired products can be made (e.g., methanol, ethylene, ethanol). There are crucial R&D needs in catalyst development and in systems-level design and development. | Figure adapted from J. Wu et al. 2013. *J-EDS* **160**(9), F953–F957. Used by permission.

The direct electrochemical and photochemical reduction of CO_2 to the one-carbon (C1) products methane and methanol and C2+ products (including hydrocarbons and oxygenates) has proven to be challenging to catalyze. There have been significant efforts in creating C2 and larger molecules *directly* via electrochemical and photochemical conversion of CO_2 and water. A breakthrough here results in process intensification where a single electrolyzer or photochemical system can convert CO_2 to a desired product without requiring the extensive infrastructure of a chemical plant. Laboratory studies have shown promisingly that a number of C2 and C3 molecules can be created using both homogeneous and heterogeneous catalytic systems; however, the selectivity and activity of the catalysts need significant improvement. Laboratory studies also have demonstrated that C1 and C2 products can be created using photochemical methods, although at modest rates and selectivities (Figures 3.8 and 3.9). Thus, there is motivation to explore new (photo)catalyst compositions and architectures to develop more active and selective materials and molecules for this reaction.

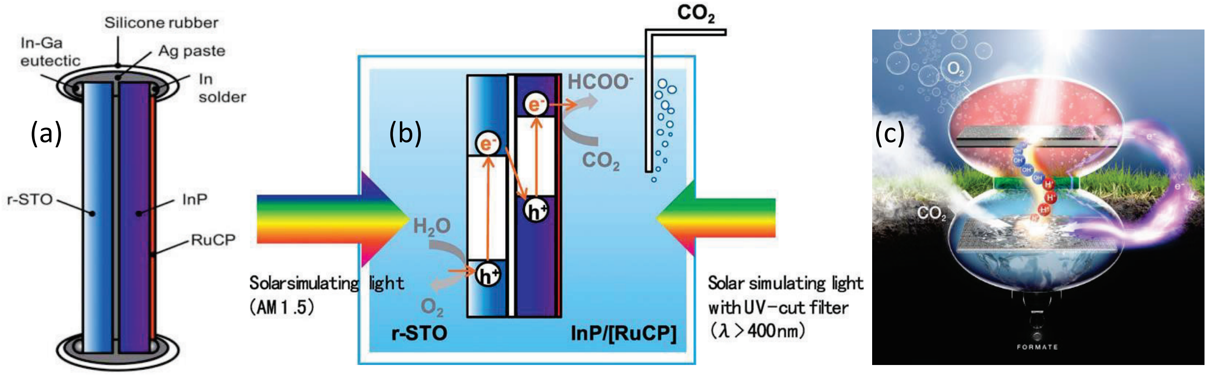


Figure 3.8. Progress toward direct solar conversion of CO_2 and H_2O to produce formate ($HCOO^-$) with no external electrical bias. Semiconductors for light-harvesting are combined with appropriate catalysts for the chemical transformations. | (a and b): Reproduced from T. Arai et al. 2013. *Energy Environ. Sci.*. **6**, 1274–1282 with permission of the Royal Society of Chemistry. (c): Adapted with permission from Zhou et al. 2016. *ACS Energy Lett.* **1**(4), 764–770. Copyright 2016 American Chemical Society

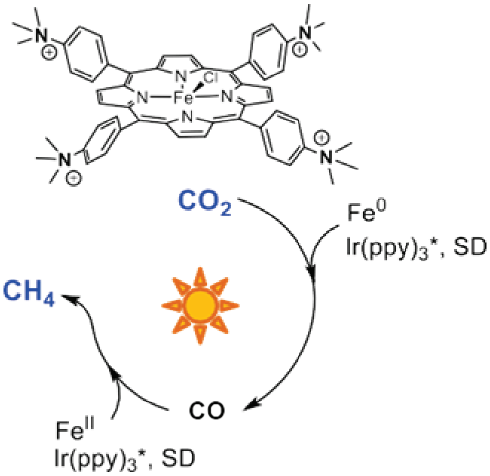


Figure 3.9. Molecular catalysts capable of producing a range of products (e.g., methane, CH_4) by electrochemical or photochemical pathways. | Reprinted by permission from Nature Publishing Group. *Nature* **548**, 74–77, Visible-light-driven methane formation from CO_2 with a molecular iron catalyst, H. Rao et al. Copyright 2017

Recent work involving computation and simulation has provided new insights that are positioning the field for successes. Theory has begun to elucidate key intermediates, descriptors, active site motifs, and ion promotion effects for these complex reaction networks, with a strong focus on understanding reaction thermodynamics. Recent developments in machine-learning algorithms have allowed these descriptors to be utilized for screening (photo)catalysts, and there are great opportunities to couple these rapid theoretical screening methods with experimental synthesis and performance testing. Advancements in microkinetic modeling have shown that the activation barriers for rate-limiting steps are nontrivial, indicating that materials discovery efforts will need to incorporate the kinetics of these sequential multi step electron and proton transfer reactions to enable accurate coupling of experiment to theory.

In addition to developments in mechanistic understanding of the (photo)catalyst–electrolyte interface, recent advancements in diffusion modeling have laid the groundwork to elucidate the complex transport phenomena occurring at longer length scales. Experimentalists have begun to explore the 3D architectures of both catalysts and their supports in vapor-fed configurations, where the reaction occurs at three-phase boundaries and an optimized flow-field is required. However, no theoretical models have accurately captured such a complicated multiphase and multiscale system, a missing gap that can be surmounted with future R&D efforts. We are at an exciting juncture in time with the development of advanced scattering, spectroscopy, and microscopy characterization techniques that are yielding unprecedented levels of information on catalysts and their surrounding reaction environment on many different length and time scales. Implementing such techniques under *operando* conditions has proven to be challenging due to the complexity of the electrified solid–liquid interface, and advancing these methods will be crucial to validating predictions. All of the aforementioned factors indicate that there are currently great opportunities to enhance our understanding of the fundamental multiscale processes that occur during electrochemical and photochemical CO_2 reduction.

3.2.2 Scientific Challenges

Utilizing CO_2 requires the addition of significant energy (~1.5 eV) by either electrochemical routes using renewable electricity or photochemical routes using sunlight to drive a series of complex proton-coupled, multielectron reactions. Significant advances have been made in using reducing equivalents (sunlight, renewable electricity) to convert CO_2 into simple molecules (e.g., CO with H_2), which can serve as feedstocks for existing or modified chemical processes and manufacturing plants. To create more complex molecules (e.g., higher hydrocarbons and oxygenates including fuels, aromatics, monomers, polymers, and carbon fibers), significant breakthroughs are needed in catalysts and materials, catalytic reaction mechanisms, and system integration. Key challenges that need to be addressed with fundamental research activity include the development of

- Scalable catalysts that exhibit high selectivity, activity/efficiency, and stability/reliability
- Novel catalytic processes that create carbon–carbon bonds
- Coupled, tandem, or cascaded reactions
- Predictive design and control of reaction pathways
- Novel materials/molecules for electrodes and electrolyzer separators
- Tools for probing and understanding reaction mechanisms at surfaces
- An understanding of degradation mechanisms and the ability to predict component lifetimes
- An understanding of transport and interfacial processes for mass, energy, and charge
- Electrolyzer designs that scale to the megawatt or gigawatt range
- Integrated approaches that reduce costs and energy requirements by combining capture, conversion, product separation, and/or reagent recycling

By making these complex processes and systems more robust, more reliable, and scalable, large-scale deployment of CO_2 utilization technology that produces CO or any other CO_2 conversion product will become a reality.

3.2.3 Why Now?

There are several key drivers for developing innovative CO_2 utilization concepts in addition to providing routes for carbon emission mitigation. Remarkable advances in the performance of solar and renewable energy provide a source of clean electricity that is increasingly available at continuously lower costs (see the sidebar “Converting CO2 with Sunlight”). Renewable electricity driven synthesis of chemicals enables the decarbonization of a broad spectrum of industries reliant on conventional petrochemicals. However, this increased penetration of intermittent renewable electricity sources such as solar and wind requires the availability of large-scale and long-term (seasonal) storage. Such storage can be accomplished only through the energy density of chemical fuels. Thus, there is ample opportunity to use clean energy for carbon utilization, and to store excess electricity as renewable carbon-based fuels. This backdrop necessitates that electrolyzer technology must scale from its current niche market (kilowatt to megawatt level) to the gigawatt level in the coming decades.

Converting CO_2 with Sunlight As Plants Do

Sunlight is the most abundant primary energy source available for the chemical transformation of CO_2, which can enable a renewable source of the fuels, chemicals, and materials demanded by society. As the reaction is energetically "uphill," it requires an energy input to make the transformation go. Photoelectrochemical transformations use sunlight directly as their energy source, just like plants, effectively an artificial version of photosynthesis. This requires semiconductors commonly studied and used in solar cells to harvest light, akin to the light-harvesting biomolecules used in photosynthesis. Both processes can convert CO_2 into useful products while also oxidizing water to make O_2. In both the natural and the artificial systems, catalysts are essential to accelerate the reactions.

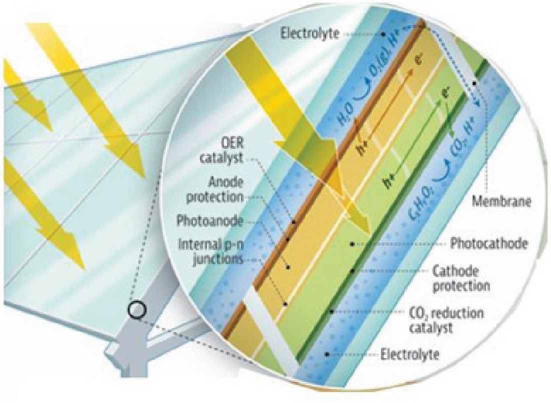


Image courtesy of Joint Center for Artificial Photosynthesis. Solarfuelshub.org

Many scientific challenges must be addressed to realize efficient, stable, long-lasting, economical structures for photoelectrochemical conversion. Now is an excellent time to leverage the tremendous advances made in solar cell research, development, and manufacturing, a technology that has recently seen explosive growth in volume and dramatic reductions in the manufacturing cost per unit area and the cost per watt of energy produced. The opportunity exists to accomplish the same for direct solar conversion processes, that is, sustainable pathways from CO_2 to the many carbon-based products (fuels, plastics, etc.) that provide a high quality of life.

The time is right to develop innovative processes owing to significant advances in several key technical areas:

- Advances in electrochemistry (e.g., modified electrodes, polymer membranes, alkaline membranes, electron mediators)
- Advances in materials discovery, synthesis characterization, catalysis science, and catalyst design through advances in theory/computation and integration with experiment
- Advances in nanomaterials science, which has matured such that new synthetic and characterization tools can synthesize and characterize atomically precise structures
- sophisticated molecular-level spectroscopy and imaging, including *operando* methods
- Major advances in synthetic biology and biomimetic approaches to create hybrid approaches

3.2.4 Conclusion

All analyses agree that conversion of light and electricity to chemicals is an important component of a sustainable energy system. Also agreed is that reaching very high penetration of renewable energy sources will be impossible without substantial deployment of chemical energy storage and conversion. The exponential growth in renewable energy generation therefore implies that the near future will present a strong market pull for chemical energy storage technology and that here CO_2 utilization must play a central role. We must embark on new scientific frontiers to develop the necessary catalysts and catalytic systems to enable efficient, highly selective conversion of CO_2 to useful products at low cost and at scale. Research and development efforts in this direction could have a substantial, positive impact on global sustainability.

3.3 Utilization Panel Report: CO_2 Conversion to Solid Carbonates

Mineralization converts carbon to a permanent solid form that is thermodynamically favored over CO_2 gas (Figure 3.10). Indeed, more than 90% of carbon on earth currently exists in this state, and ultimately the long-term geological fate of anthropogenic carbon will be in mineral form. The past decade has seen incredible progress in advancing the understanding of, and technology for, capturing and converting CO_2 into solid mineral-based materials. Most prior research has focused on the investigation of in situ mineralization of CO_2 in geologic formations with magnesium and calcium-bearing minerals [Gadikota et al. 2014]. Ex situ mineral carbonation has also been developed to chemically and physically accelerate mineral carbonation rates [Park et al. 2003; Park et al. 2004; Zhao et al. 2013; Swanson et al. 2014; Pan et al. 2018].

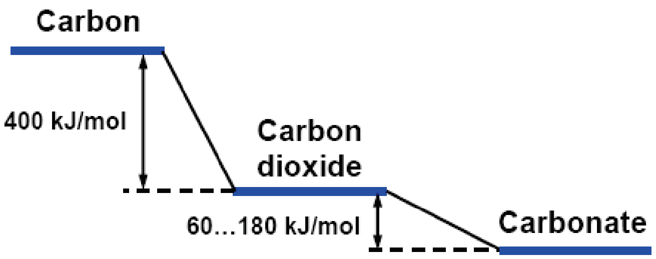


Figure 3.10. Thermodynamics of carbon mineralization. | Image courtesy of Ah-Hyung Park, Columbia University

As shown in Figure 3.11, the most abundant materials that can fix gaseous CO_2 into solid carbonates are silicate rocks. In addition, a wide range of industrial wastes, such as steel slag and fly ash, contain alkaline metals. The use of these industrial wastes in ex situ carbon mineralization is interesting because they often coexist with industrially emitted CO_2. Thus, the energy-intensive transportation of feedstock can be eliminated.

The ex situ carbonation of silicate minerals and alkaline industrial wastes can lead to co-production of valuable byproducts (e.g., high-surface-area silica, iron oxide, and extracted rare earth elements) and the chemical and physical properties of solid carbonates can be tuned during the carbonation process to match various applications. For example, carbonates and other byproducts can be used as construction materials, which generally have high environmental footprints. A built environment that uses CO_2 from fossil fuel combustion on a scale commensurable with historical anthropogenic emissions could potentially achieve the net negative emissions. It can also displace energy-intensive and environmentally unfriendly raw material feedstocks by incorporating industrial waste streams into product fabrication.

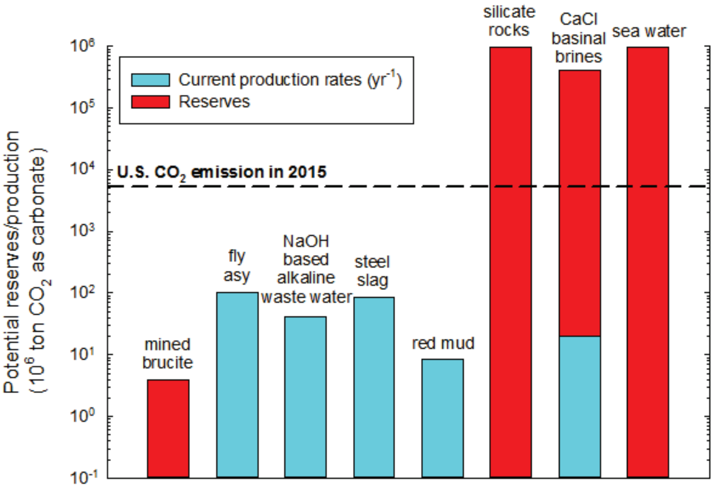


Figure 3.11. Various feedstocks for carbon mineralization. | Image prepared by Ah-Hyung Park, Columbia University using data from H. Xie et al. 2016. *Environ Earth Sci* 75 and The Statistics Portal

A recent market assessment determined that carbonate mineral-based construction materials could reach annual revenues of $1 trillion and the potential to consume 3–6 GT of global CO_2 emissions by 2030 [Global CO_2 Initiative 2017]. To achieve this, many different industrial feedstocks and building products are envisioned that share common production pathways and processes. In nature carbon mineralization is generally considered a slow phenomenon, but in industrial products it has been observed to proceed at rates orders of magnitude faster than predicted by conventional models.

We currently lack a fundamental understanding of this dynamic and highly heterogenous reaction system for effective mineral carbonation, but there is consensus that the key to transformative advance lies in optimizing surface reactivity and mass fluxes across mineral–liquid–gas interfaces. To realize the potential of both in situ and ex situ carbon mineralization for carbon storage as well as carbon utilization, we must be able to model and control reaction pathways and rates to accurately estimate carbon storage and utilization potentials and to meet product performance criteria.

3.3.1 Status of CO_2 Conversion to Solid Carbonates

Carbon mineralization (Figure 3.12) encompasses a complex set of reactions by which CO_2 reacts with a Ca, Mg, and/or Fe oxide bearing phase (MO = metal oxide) leading to the formation of the corresponding solid carbonate phase (MCO_3). A specific feature of this carbon utilization pathway is that the overall reaction is exothermic (e.g., the enthalpy of reaction of CaO to $CaCO_3$ is 90 kJ/mol).

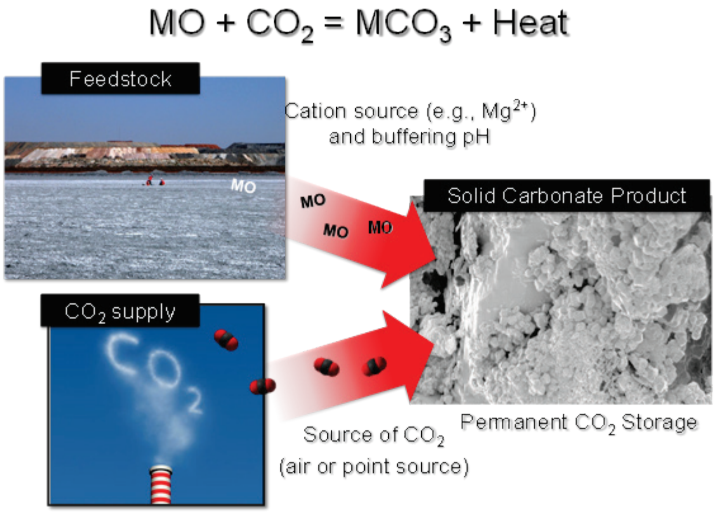


Figure 3.12. Conceptual framework for carbon mineralization. | Image courtesy of Greg Dipple

Solid carbonate products can be tailored for physical and chemical properties and applications by controlling feedstock, reaction pathways, and system and heat integration (Figure 3.13). A gas–solid process at high temperature can be exploited for enhancing the carbonation kinetics of Ca oxide phases and presents the advantage of not requiring wastewater separation and processing, which presents additional costs and environmental burdens. At ambient conditions carbonation proceeds via a gas–liquid–solid pathway. Carbon dioxide and reacting metal oxides dissolve in the liquid phase from which carbonates precipitate. Mine waste processing and cement curing are examples of processes employing low liquid-to- solid ratios (wet or thin film routes). For other applications in which the goal is to maximize CO_2 storage or produce high-value products with greater purities, ex situ slurry phase processes are preferred.

Aqueous mineral carbonation can be carried via direct and indirect pathways (Figure 3.13). Direct carbonation refers to processes whereby the extraction of mineral ions from the feed material and the carbonation reaction occur simultaneously as a single step. At elevated temperatures and pressures, conversion is rapid; whereas at ambient conditions, such as in mine waste piles, direct conversion proceeds at a slower pace but on a scale of millions of tons, considering the large amounts of material that can take part in the reaction under in situ conditions. On the other hand, carbon mineralization via the indirect route involves two or more stages. It requires the extraction of mineral ions from the feed material (dissolution) as a preliminary procedure prior to magnesium carbonate precipitation. By separating the dissolution and precipitation steps, carbonation can be completed under milder conditions because of the independent optimization of each step. This leads to an enhancement of the overall carbonate conversion rate while also generating a product with a higher purity and hence potential for utilization. Acceleration of the dissolution step can be achieved through energy-consuming pretreatments (e.g., heat activation), chemical additives (e.g., Mg, Ca and Si-targeting ligands [Park et al. 2003; Park et al. 2004; Zhao et al. 2013; Swanson et al. 2014; Pan et al., 2018]), and carbonic anhydrase (biocatalyst [Patel et al., 2013]). In the case of chemically and biochemically enhanced carbon mineralization, the recyclability of the chemical additives would be one of the critical factors for economic feasibility.

The direct route is best suited to treating pure and concentrated CO_2 streams, whereas the indirect approach can be applied to both concentrated and diluted CO_2 streams, including untreated flue gases. Consequently, engineered carbon mineralization technology has prospective applications in mineralizing CO_2 emissions from fossil fuel–based power generators and other high-intensity CO_2 emitters such as natural gas producers and oil refineries; chemical and fertilizer production plants; nonferrous metal, iron, and steel production facilities; and cement plants.

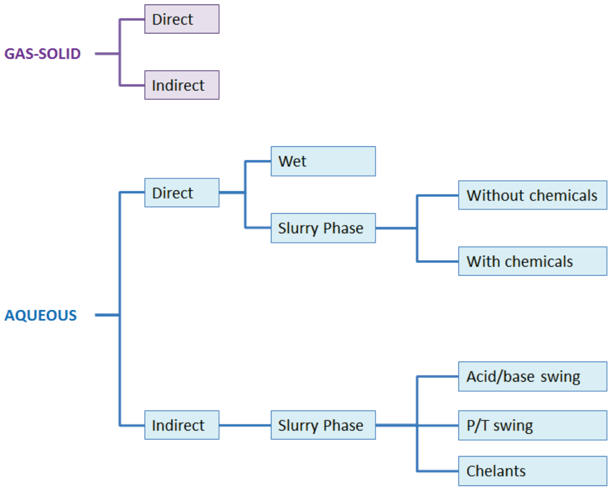


Figure 3.13. Main process routes for carbon mineralization. | Reprinted by permission from Springer Customer Service Centre GmbH: Springer, *Transformation and Utilization of Carbon Dioxide,* B. M. Bhanage and M. Arai, eds. Copyright 2014. R. Baciocchiet al. 2014. Accelerated carbonation processes for carbon dioxide capture, storage and utilisation, pp. 263–302. Green Chemistry and Sustainable Technology series. L.-N. He et al., series eds.

Exploring the range of potential feedstocks for carbon mineralization

As discussed earlier, the largest carbon mineralization potential lies with natural silicate minerals. But there are many industrial processes producing reactive materials and CO_2 gas streams at a scale commensurate with large-scale solid mineral carbonate formations [Bobicki et al. 2012; Power et al. 2013]. The industrial environments and feedstocks are highly variable, but all share alkaline reaction conditions and similar reaction pathways. In this section, the discussions focus on mineral and industrial wastes that are readily available for CO_2 utilization and storage. The reaction mechanisms and kinetics discussed here can also be used to provide insights into in situ carbon mineralization occurring in geologic formations into which CO_2 is injected to be stored.

Magnesium-rich ores from mining can be used as feedstocks for carbon mineralization, including dunite, harzburgite and serpentinite, composed primarily of silicate minerals (e.g., olivine, serpentine, pyroxene). These ores liberate magnesium in the form of cations in aqueous media, which subsequently react with CO_2 to form the carbonate solid product. The reactivity of silicate minerals is enhanced through pretreatment, either in the form of grinding, as in mine waste, or in the form of thermal activation to elevated temperatures (some as high as 700°C) [Gerdemann et al. 2007]. The substantial, established reserves of these ores (in theory sufficient to mineralize all anthropogenic sources of CO_2), and the possibility of producing products of commercial value following reaction with CO_2, make this utilization technology appealing. However, one important, fundamental challenge for the successful development of carbon mineralization utilizing mineral ores as feedstocks is to explore novel pretreatment or chemical and physical activation schemes that engender the reaction of the mineral ore with CO_2 but, in doing so, consume less additional energy. The dissolution of the silicate minerals results in a silica-rich passivation layer that limits the overall conversion. Thus, an understanding of the reaction kinetics and mechanisms associated with the transition from the surface reaction kinetic limited reaction regime to the mass transfer limited regime is important to optimize the extent of the carbon mineralization for various minerals.

Alkaline mine waste and tailings generated by the mining of nickel, chrome, platinum group metals, diamond, chrysotile, copper, and gold are also reactive with CO_2 for carbon mineralization. The use of tailings in accelerated applications is geographically limited to mine sites situated within a few hundred kilometers of CO_2 point sources. The most studied tailings are those mainly composed of ultramafic rocks, because of their high storage potential (around 0.40 t CO_2/t). Experiments with serpentinite-based residues showed promising carbon mineralization rates from both concentrated and pure CO_2 streams under aqueous conditions. Combination with metals extraction and value-added products increases the potential application of such routes [Pasquier et al. 2016]. Red mud (bauxite residue) generated by alumina processing also has carbonation potential and has been well studied, as it addresses the environmental issues associated with the high alkalinity of these residues.

Direct capture of CO_2 from air by reaction with mine waste has been documented in a number of mine times and climate environments. This in situ passive carbon mineralization process binds carbon within mineral precipitates [Power et al. 2013]. Reaction proceeds because the host rocks to ore are formed at depth within the earth and the minerals therein are out of chemical equilibrium with the atmosphere. Documented rates of CO_2 uptake at mine sites in Canada, the United States, Australia, and Norway range from 0.3 to 6 kg CO_2/m^2 per year, which is 2–5 orders of magnitude greater than natural weathering rates for Earth's major river catchments.

Alkaline industrial solid residues are highly reactive with CO_2 because of their formation at high temperature and high surface areas from comminution. Their co-location with large industrial CO_2 emitters (Figure 3.14) reduces transportation requirements. Economic co-benefits include the immobilization of potential contaminants and extraction of high-value commodities such as rare earth elements. Direct, indirect, dry, wet, and aqueous processing routes have been tested, giving a broad portfolio of application opportunities. Similar process pathways exist for the treatment of waste concrete, coal fly ash, cement kiln dust, paper mill waste, municipal solid waste incineration residues, and even asbestos wastes [Pan et al. 2012]. Steel-making by-products, including basic oxygen furnace and electric arc furnace slag, are derived from the reaction between flux materials (e.g., limestone and dolomite) and the silica/silicate impurities in iron ore. The major constituents of slag include CO_2-reactive phases such as calcium-containing silicates, CaO (i.e., free lime), and MgO. In terms of abundance and reaction rates, slag is one of the most promising feedstocks for carbon mineralization. In addition, its high CaO content hinders direct use in bound building materials, since it causes a decrease in durability due to hydration and swelling when exposed to moisture. Carbon dioxide treatment and conversion to carbonates circumvents these issues, thereby increasing the utilization potential of the slag. Several types of process routes have been tested, including a gas–solid route to be applied directly on slag as it is poured out of the furnace [Santos et al. 2012].

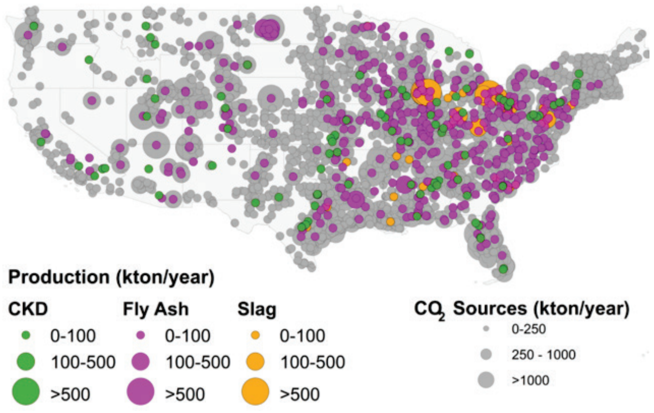


Figure 3.14. Industrial sources of residues (CKD: Cement Kiln Dust and stationary sources of CO_2 in the US).
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Brines are a class of wastewater that contain elevated levels of undersaturated salts (such as chlorides, nitrates, and soluble sulfates), and at times ultrafine solid particles (such as colloidal and clay-sized particles) not separable by low-cost gravitational or filtration methods. The value of alkaline brines for carbon mineralization is in the substantial quantities of calcium and magnesium (and occasionally strontium) that can trap low-pressure impure CO_2 as soluble bicarbonates or be precipitated as solid carbonate minerals. During carbonation, the alkalinity of these brines is neutralized. Buffering additives (e.g., NaOH, $NaHCO_3$, carbonic anhydrase enzyme) are therefore often required and present a major challenge for the technology since their recovery and recycling is difficult and costly. On the other hand, alkaline brines are widely available around the world, as they are associated with diverse activities such as aluminum production, oil and gas extraction, power generation facilities, and seawater desalination. This means that brines have a significant capacity to store CO_2 and also a relevant potential to produce value-added products, such as fillers and pigments for paper, polymers, and coatings. Carbonation of oil/gas brines also leads to co-precipitation of toxic heavy metals (e.g., Pb, Ni, Zn), which reduces the environmental impact of brines discharged into surface or subsurface waters.

Addressing the different types of products and applications of carbon mineralization

Direct and indirect carbon mineralization of various natural and industrial alkaline materials offers the opportunity to produce a range of tailored carbonation products and by-products as construction and building materials [Zhao et al. 2013; Gadikota et al. 2015]. Process adaptation or post-processing can be employed to further expand the range of products to include higher-value ones. Applications include structural materials (e.g., cements, concrete, and mortars), nonstructural materials (e.g., for road-base, erosion, sea, and flood protection barriers), and calcium- and magnesium-based carbonates that may be used for different applications (e.g., as additives for protective coatings such as paints and polymers). A scheme of carbon mineralization and of the range of its products, which depends on feedstock, operating route, and reaction conditions, is reported in Figure 3.15. In construction applications carbonate solids can provide cementitious binding of the components of the building product, or structural support (as an aggregate or filler). Furthermore, the carbonation of alkaline industrial waste may also be applied to immobilize or extract heavy metals, stabilize chemically metastable mineral phases, or even store energy or provide carbon to microalgae.

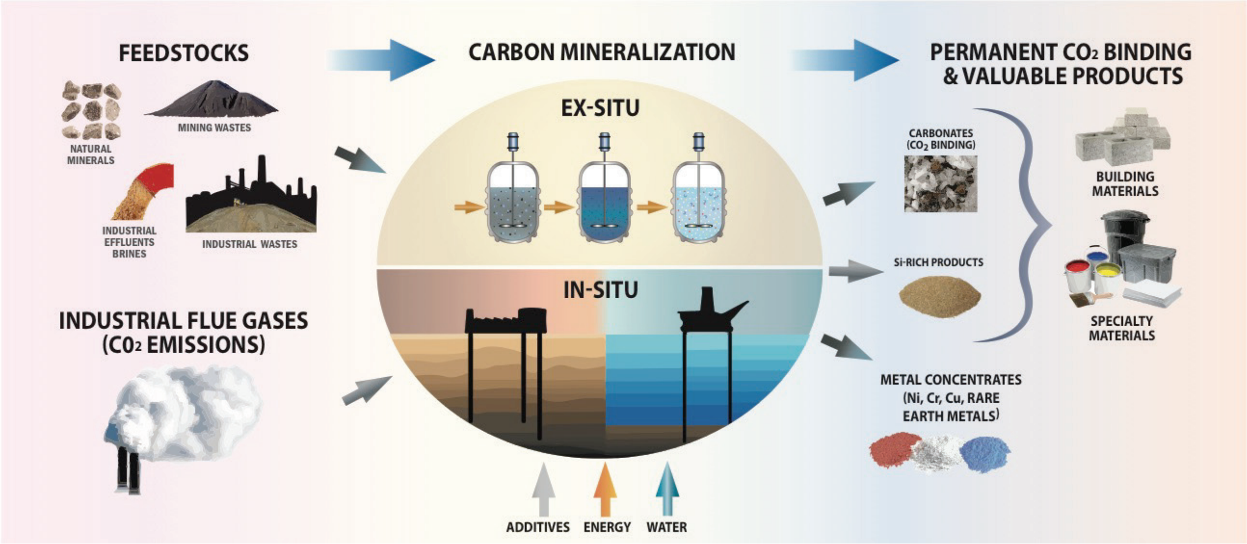
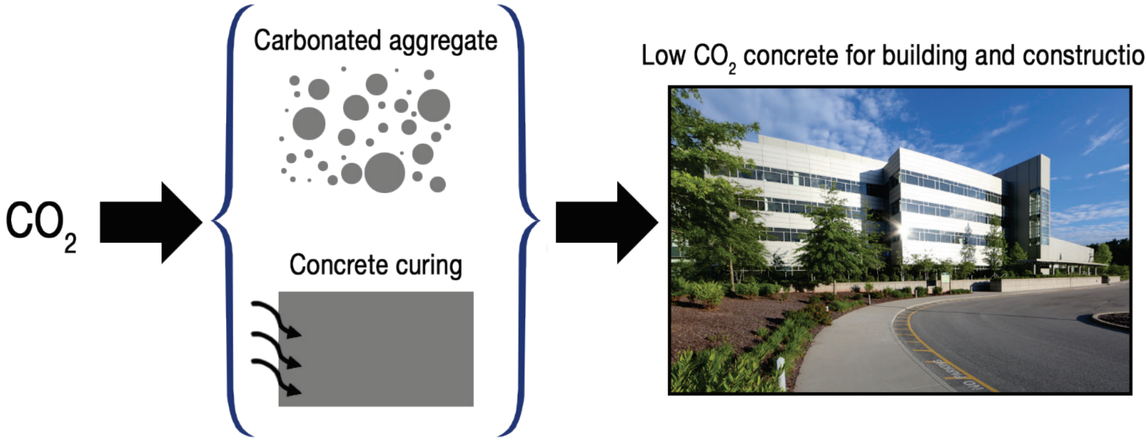


Figure 3.15. Scheme of carbon mineralization and of the range of its products. | Image courtesy of Florent Bourgeois, Laboratoire de Génie Chimique; Au-Hung Park and Xiaozhou Sean Zhou, Columbia University

The building sector presents a very significant carbon footprint (see the sidebar "The Concrete Sector"). Thus, the application of carbon mineralization processes to some of the alkaline materials used in construction may not only allow products with improved technical properties but may also exert an impact in terms of CO_2 emissions reduction. Carbon dioxide utilization has entered the **cement and concrete** segment from a variety of technical approaches (e.g., [Jang et al. 2016; Zhang et al. 2017]). Calcium silicates, both within traditional Portland cements and novel nonhydraulic cements, readily react with CO_2 to form calcium carbonate. The reaction leads to hardening and solidification of the treated binder. Traditional precast concrete masonry products lend themselves to CO_2 curing that complements or replaces conventional moist curing. Ready-mix concrete using CO_2 as an admixture improves compressive strength. In addition, aggregates formed through carbon mineralization of alkaline waste can displace natural aggregate input into concrete and hence further reduce CO_2 emissions. For this latter application carbon mineralization is employed in a cold-bonding granulation process, during manufacturing and/or curing under a CO_2 rich atmosphere, to produce **synthetic aggregates** from different types of residues (such as waste incineration fly ash and steelmaking slag). Another example of application of carbon mineralization in the building sector is the manufacturing of blocks or compacts containing finely milled steel slags that, by CO_2 curing at elevated temperature and pressure, achieve high mechanical performance without the use of cementitious binders and also a relevant permanent storage of CO_2 [Quaghebeur et al. 2015]. Adequate compression strengths were alternatively obtained by CO_2 curing under ambient conditions, reducing the slag content. Carbon mineralization may also be applied as a treatment technique to improve the environmental behavior (i.e., leaching properties) of waste materials, such as incineration bottom ash, to allow their use as aggregates or filler materials.

The Concrete Sector: Great Potential for Carbon Mineralization



(Left): Image courtesy of Timothy Oliver. (Right): Image courtesy of Oak Ridge National Laboratory.

Concrete is a mixture of Portland cement with sand and gravel aggregate. Cement production exceeds 4 billion tonnes per year with a carbon footprint of about 800 kg CO_2 per tonne of cement, making it the largest contributor in the industrial chemical sector. It contributes 5–7% of global anthropogenic CO_2 production and thus has the potential for reducing anthropogenic CO_2 emissions significantly (estimated at 1–2 billion tonnes per year).

Through carbon mineralization, CO_2 emissions from cement manufacturing could be used for the production of concrete. The CO_2 can be mineralized using a variety of feedstocks producing carbonated aggregates. These aggregates can be used to manufacture concrete or concrete-based building materials, hence replacing gravel aggregates.

CO_2 emissions from cement manufacturing can also be used in the curing of concrete. The introduction of CO_2 into the curing process promotes carbon mineralization reactions. The mineralized CO_2 is incorporated into the concrete matrix, enhancing strength. The strength benefits available through carbon mineralization present an opportunity to reduce the amount of cement used for an equivalent strength-grade concrete.

Reduction in the carbon footprint of concrete through mineralization of CO_2 has promise to transform the built environment without sacrificing the quality of construction materials.

An additional desirable outcome for carbon mineralization is to engineer processing pathways that simultaneously extract metal value from such feedstocks while binding CO_2 to the feedstock material itself. The underlying concept uses CO_2 from flue gases to extract metal phases from such feedstocks. The process could be referred to as **enhanced metal recovery** (EMR) (see the sidebar **"**Enhanced Metal Recovery"), in that it has some similarity to enhanced oil recovery (EOR). This concept adds economic value to carbon mineralization associated with both metal concentrate and carbonate production, the latter being tied to the production of building materials. For example, new production pathways using CO_2 as a reactive agent to process nickel laterites would produce both nickel and carbonate building materials. Similar approaches could extract rare earth metals from existing stockpiles of mining waste. EMR, applied to primary mineral resources, could be envisioned ex situ and/or in situ. The carbonated products could then be used for producing building materials, or they could be left in the ground. An alternative deployment would use carbonate solid precipitates to bind and immobilize deleterious metals and materials (e.g., asbestos) within mine waste and the use of EMR for ex situ carbon mineralization using silicate minerals and alkaline industrial wastes that contain valuable metals and rare earth elements.

Implementing an ex situ indirect process route can produce **high-purity mineral carbonates**, such as precipitated calcium carbonates or precipitated magnesium carbonates, which have even greater value as a chemical feedstock for paper and paint production, displacing resource extraction routes for conventional materials [Zhao et al. 2013; Fricker et al. 2013; Fricker et al. 2014].

Hydrated Mg-carbonate minerals produced through carbon mineralization of brines and alkaline solids have high solubility, which facilitates their use as a **carbon storage and transport medium**. An innovative carbon mineralization process consists of capturing CO_2 into hydrated minerals to be provided to microalgae as a supplement. Microalgae have the potential to significantly intensify biofuel production processes, but their growth requires carbon. CO_2 can be supplied as a gas either with high purity or as a flue gas. However, in the absence of a point source of CO_2, carbon may be supplied to the algae through the dissolution of carbonate minerals. A similar novel process may exploit the large enthalpy of hydrated Mg-carbonate minerals' dissolution–precipitation cycles to **store energy** or serve as a pathway to capture CO_2 from dilute or dirty sources and convert it to a high purity stream for other utilization processes.

3.3.2 Scientific Challenges

Carbon mineralization presents great potential as a permanent CO_2 storage treatment and for obtaining products and materials that may be used for other applications. However, to achieve high reaction rates, material pretreatment, enhanced operating conditions, and the use of precaptured CO_2 (or reagents and additives) have generally been reported to be necessary, thus leading to processes generally reputed too energy intensive and costly.

With regard to in situ carbonation of mine tailings, the rates and extent of carbon mineralization are limited by the availability of CO_2. Thus, enhancing the delivery of CO_2 to reaction sites is a priority for maximizing the benefits of this approach. Enhanced delivery of CO_2 is expected to push these systems to the limits of cation availability, but our ability to deliver CO_2 is limited by mass transfer rates within alkaline mineral–fluid–gas systems. For some mines, this limit may be on par with the greenhouse gas production associated with mine operations, opening up the possibility that some mine operations could become greenhouse gas neutral. As CO_2 delivery limits are overcome, the next limit to carbonation rates will be imposed by the rate of metal extraction from the mine waste feedstock. Activation of feedstock can dramatically improve reaction performance, but surface control of these reactions is poorly understood.

Concerning the application of carbon mineralization in the building sector, the key issue is meeting and guaranteeing product performance over time. The basic issues that thwart its adoption involve the extensive standard testing methods required to ensure that the new materials are safe to use for a range of infrastructure or building applications. These tests are expensive and time consuming, requiring months or years of analysis. Another obstacle is uncertainty in long-term performance. When carbon mineralization introduces new chemical bonding characteristics, a thorough understanding of the fundamentals of the binding reactions and their long-term stability is a prerequisite to formalizing performance testing.

Enhanced Metal Recovery and CO_2 Utilization and Storage

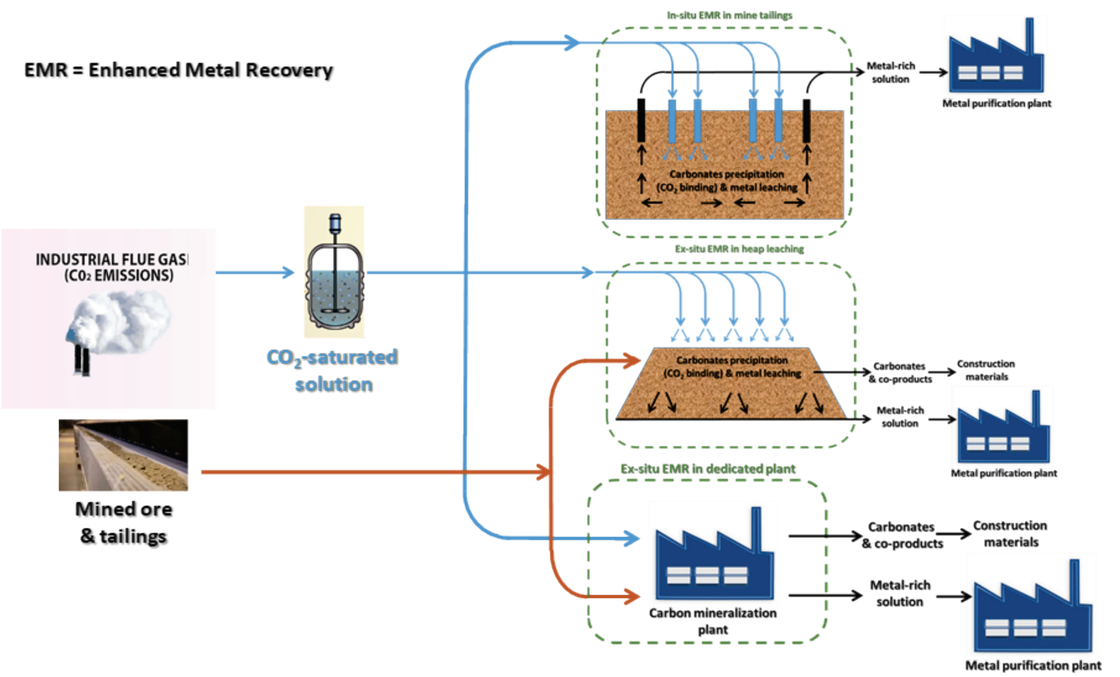


Image courtesy of Florent Bourgeois, Laboratoire de Génie Chimique

Feedstocks for carbon mineralization—such as silicate ores, mine tailings, and industrial residues like steel slag—typically contain many metals of value, such as iron, nickel, vanadium, chromium, platinum, and rare earths. An innovative application of carbon mineralization referred to as enhanced metal recovery (EMR) exploits this process to store CO_2 as mineral carbonates and to recover valuable metals. The reaction of the alkaline feedstocks with dissolved CO_2, an acidifying agent, releases elements such as magnesium, calcium, or lithium, as well as other valuable elements (e.g., rare earth elements) into solution.

As illustrated in the image, three potential EMR routes are envisioned:

1. In situ, in which a CO_2-saturated solution is injected into geologic formations.
2. Ex situ EMR as a heap leaching process, by which a CO_2-saturated solution is fed to heaps of industrial residues or mine tailings.
3. Ex situ EMR in a dedicated processing plant, employing either direct or indirect carbon mineralization reactions. Reaction conditions can be egnineered depending on the types of feedstock and metals that are to be extracted.

In all EMR routes, CO_2 is bound to the carbonate product, which is either valorized, for example, as a construction material (for the ex situ cases,) or bound in the ground (in situ route). The metal-rich solution is subsequently processed by hydrometallurgy to recover the metals and metalloids. In EMR, the carbon mineralization costs may be partially offset by the value of the recovered metals.

The current state of the art of carbon mineralization use in construction is limited to precast building materials and nonreinforced applications. The implementation of carbon mineralization may have a big breakthrough if the technology is adapted to replace the cement binder in ready-mix concrete and in reinforced (concrete) building applications. To reach this goal further improvements of the carbonated products regarding mechanical behavior and environmental quality are necessary. Our poor understanding of surface reactivity and mass fluxes in cement is reflected in the large variability of cement formulations by location and climate, developed largely on an ad hoc basis. This lack of a fundamental understanding hinders the large-scale adoption of CO_2 in concrete production. Another obstacle to realizing CO_2 utilization is elemental and phase impurities, which can both accelerate or hinder the carbonation reaction. Incorporating an industrial feedstock such as slag or mine waste as aggregate in concrete while generating environmental benefits only complicates the complexity of chemical and physical interactions, including, but not limited to, altering reaction chemistry, obstructing mass transport, deregulating dissolution rates, crystallizing unexpected impurity phases, or immobilizing important reactive components such as CO_2. Hence, again the elucidation of the microscale phenomena occurring during carbon mineralization processes is fundamental.

Also with regard to the use of carbon mineralization as a carbon storage and transport medium (e.g., for microalgae cultivation), a well-constrained process must be performed. In particular, optimal thermodynamic conditions for precipitation and dissolution must be identified, and the kinetics of precipitation of hydrated minerals within a brine and their dissolution in the presence of algae must be characterized.

Carbonation reactions occur at the interface of solid–liquid–gas systems and can evolve near or far from equilibrium conditions. The thermodynamic properties and reaction rates may hence present wide variability depending on the operating conditions. Many of the materials being utilized and precipitated lack basic thermodynamic characterization, which hinders even fundamental predictions of phase behavior and final state. This is further complicated by the generation of surface reactivity through pretreatment. In addition to these kinetic controls on rate, mass fluxes are highly variable and can be controlled by transfer across phase boundary interfaces (gas–liquid, liquid–solid). Feedstock composition and mineralogy are very material specific—even sample specific—both for residues and rocks and may vary over time due to interaction with the environment and surface passivation. Mineralogy is a key parameter for CO_2 feedstock reactivity and affects the release in solution of major components and trace contaminants such as metals and metalloids, thus impacting product properties and valorization potential. Even trace amounts of chemical constituents and mineral phases can profoundly alter reaction pathways and rates.

The challenges of carbonation research thus primarily come from the complexity of the mineral system, which contains not only various cations (Ca/Mg/Si) but also compounds with different states of carbonation and hydration [Zhang et al. 2017]. The thermodynamics of carbonation are first principle, which determines the required composition and partial pressure of feedstock, degree of carbonation, and properties of the product. The transport direction and potentially maximum flux of the process (e.g., ion leaching [Sanna et al. 2014], interfacial water mitigation [Wang et al. 2017], and heat transfer) are also necessary data that can be attained by thermodynamic tools.

Multiscale geochemical thermodynamic models that cover leaching processes, interfacial water transportation, and mineral carbonation at microscale, mesoscale, and macroscale need to be systematically addressed. High resolution experimental systems based on spectrum analysis and calorimetric analysis need to be developed for thermodynamic data characterization and thermodynamic model validation [Longo et al. 2015]. Multiple conditions (e.g., pH, high temperature, high pressure, gas species) should be analyzed in the experimental system. Furthermore, the building of a thermodynamics database with standard data format is necessary for scientific data analysis and sharing.

Another challenge in the field of carbon mineralization has been a lack of fundamental molecular-scale understanding of the adsorption and speciation behaviors at complex solid–fluid interfaces. Recent development of more robust force-fields such as CLAYFF [Cygan et al. 2004] have enabled us to develop an advanced understanding of diffusive transport, sorption, and ion exchange behaviors at solid–fluid interfaces. Advanced computational tools such as molecular dynamics, Monte Carlo, and density functional theory can be applied to investigate gas–fluid–solid interactions at complex mineral interfaces, which are challenging to determine using conventional materials measurement techniques. Emerging research frontiers in the area of carbon mineralization include developing convergence in predictive behaviors using advanced computational tools, and synchrotron and neutron scattering and spectroscopic measurements.

The elucidation of carbon mineralization reaction pathways and rates with regard to solid feedstock/fluid/CO_2 systems can also be achieved through the use of online high-resolution investigative tools. These tools are becoming broadly available, and there is a genuine urgency for their deployment in the carbon mineralization research field.

As for further specific research topics that should be addressed in the carbon mineralization field, more effort is needed to find or develop additives for enhancing carbon mineralization kinetics that can be regenerated energy-efficiently, so as not to hamper the whole process in terms of costs and overall environmental impacts (e.g., greenhouse gas emissions associated with regeneration or additive production). Learning from a natural process may inspire the development of innovative ways to enhance carbon mineralization. Even if carbonation involves the combination of two inorganic compounds (CO_2 and alkaline earth metal oxide), it is not an exclusively inorganic process. There are also biological routes that generate solid, stable alkaline carbonates. Mollusks are an obvious example, taking the inorganic building blocks from water and turning them into aragonite- and calcite-rich mineralized tissues (i.e., shells). There are also algae, microorganisms, and a host of invertebrates and vertebrates that can induce the formation of calcium- and magnesium-carbonates, either through endogenic or exogenic pathways. Hence, biological routes to carbon mineralization should also be considered, using active biological agents or bio-derived substances (e.g., enzymes such as carbonic anhydrase, and other organic macromolecules). Besides the use of biology and biochemistry, biomimetic routes might be developed to mimic the local chemistry and mass transport mechanisms that organisms use in building their well-structured and complex tissues. This could lead not only to novel routes for accelerated carbon mineralization, but also the production of novel bio-inspired materials.

Furthermore, a significant breakthrough for the application of carbon mineralization would be achieved by the development of an integrated technology capable of obtaining a product with suitable properties for utilization and also significant CO_2 uptake, employing flue gas (or other diluted CO_2 sources such as syngas and biogas from anaerobic biodegradation processes). This could be performed by contacting the enriched CO_2 stream directly with the feedstock or with the alkalized mineral solution obtained by dissolution of the reactive phases at optimized conditions. This type of process is particularly challenging as CO_2 in flue gas is present at low concentrations and contaminated with NOx, SOx, and other pollutants. It could be carried out for the beneficiation of ultramafic feedstocks and ores or other types of industrial residues such as steel slag and should be optimized to maximize carbonate yields within timeframes associated with CO_2 capture in aqueous phase.

3.3.3 Why Now?

While geologists have long studied natural weathering phenomena to explain geological events, only recently has carbon mineralization become an industrially relevant process. Because of this history, carbon mineralization was originally seen as a slow process; in fact, CO_2 was long considered an unreactive species. What we now know is that under the right conditions, carbon mineralization occurs much more rapidly, and therefore can be used to sequester CO_2 at the same rate as, or even faster, than CO_2 generated anthropogenically. Those right conditions, however, are elusive. They occur momentarily in chemical reactors, but rates rapidly decay due to mass transfer barriers. They occur in ambient systems, but unexpectedly, and have not been replicated in engineered systems.

These insights have been shared among the scientific community since roughly 2006, when the first International Conference on Accelerated Carbonation for Environmental and Materials Engineering was held. At the time, key research themes included explaining the natural weathering of alkaline minerals, building materials, and wastes, and developing methods to replicate these phenomena in an accelerated manner at lab scale, for the purpose of understanding their mechanisms and effects. A few editions later, the focus shifted toward CO_2 sequestration to mitigate industrial emissions, and most recently, utilization has become the main research driver. Besides technical advances and novel ideas, the focus has shifted toward products, as carbon credits cannot presently justify the operation of the industrially oriented processes so far developed; therefore, carbon mineralization products are the real asset of this process.

The first few industrial implementations of carbon mineralization have recently begun operation, but their carbon utilization capacity is limited, mainly because the performance risk of the commercial products is too high, or because the most reactive feedstocks are available in limited quantities. Efforts are therefore urgently needed to enable the adoption of more widely available, but less reactive and mineralogically and chemically complex, feedstocks for the intended applications. Efforts are also needed to develop mechanistic and multiscale understanding of carbon mineralization reactions, to overcome the existing rate and conversion limitations, and to open opportunities for better-tailored products and by-products. Finally, to obtain this new understanding, concerted and scientifically sound efforts are needed to generate comprehensive databases of reaction kinetics data; transport phenomena coefficients; and fundamental chemical, thermodynamic, and physical properties.

While challenging, addressing these timely topics is now within grasp as a wide range of advanced characterization tools that can provide the insights and data needed (such as real-time particle size, shape, and crystallinity analysis; Raman spectrometry; x-ray diffractometry; x-ray tomography; and x-ray absorption, among others) have recently been developed and are becoming accessible to the wider carbon mineralization community. Likewise, molecular modeling techniques and computational tools to express them have become increasingly accurate and reliable, and experimental techniques to generate high-resolution time- and scale-dependent data have arrived and can be readily exploited, with the right resources.

3.3.4 Conclusions

Carbon mineralization as a pathway to utilization presents multiple potential assets: it allows CO_2 to be stored in a permanent solid form, improves the properties of alkaline waste materials and/or construction materials, and provides products for different applications and even for transport and temporary storage of carbon and/or energy. Carbon mineralization systems and their thermodynamic and kinetic multiphase behavior are not, however, sufficiently understood to allow the design to be optimized for energy-efficient applications. The tailoring of carbon mineralization processes for different types of feedstocks aimed at achieving specific products/applications may be achieved only upon a deep understanding of carbonation systems and the reactions that occur within.

Being able to predict the dynamic speciation of major and trace elements during treatment and the product properties of solid feedstock/CO_2 systems in aqueous or gas systems is key to identifying and controlling carbon mineralization reaction pathways and rates. Current models cannot reproduce the most basic processes observed in experiments. To overcome these constraints, fundamental research is necessary to derive insight into the interaction among solid, liquid, and gas phases. Controlling bulk physical and chemical properties during the production process by real-time monitoring of the gas and liquid permeability of the compact and carbon mineralization product properties is absolutely necessary to optimize the overall reaction and obtain a product responsive to specific performance criteria. The achievement of this objective would result in a large capacity to generate construction and building materials based on the use of gas streams rich in CO_2, which would hence be permanently stored and not emitted into the atmosphere.

3.4 Utilization Panel Report: Biological CO_2 Utilization

Biological CO_2 conversion is fundamental to all life on Earth, as it contributes to the synthesis of numerous compounds. With the rise of agriculture, humans have harnessed the ability of plants to produce crops using carbon taken from the atmosphere. However, we are yet to fully exploit the power of microorganisms to convert CO_2 into useful products. Microorganisms have long been used for the production of foods and beverages, and in the last century their ability to produce fuels, chemicals, and pharmaceuticals has been industrialized. These processes largely rely on the conversion of complex organic substrates such as sugars, which are derived from harvested crops. However, many microorganisms can utilize CO_2 or other C1 substrates directly to produce feed, fuels, and base chemicals. Collectively, these conversions are known as C1 metabolism. There is vast untapped potential to use these microorganisms in engineered bioprocesses to create such products from C1 intermediates, which include CO_2, carbon monoxide (CO), and formate (HCOOH), captured directly from the atmosphere or from more concentrated industrial sources. These products can displace those derived from fossil carbon, thereby reducing net carbon emissions. Replacing fossil fuels with low-carbon fuels as a source of stored energy is a very large potential market that would result in significant reductions to net CO_2 emissions. Intensified microbial production of protein feeds and base chemicals would also help address problems involving water, land, and fertilizer use.

For all biotransformations of CO_2 into products, energy is necessary to chemically reduce the carbon. For this, photoautotrophic microorganisms use sunlight, and chemolithotrophic microorganisms use chemical energy (Figure 3.16), which can be sourced from renewable electricity or industrial waste streams.

The utilization of C1 intermediates via microbiological processes is promising for these reasons:

- A range of valuable products can be produced, including feed, fuels, and base chemicals.
- C1 intermediates are abundant.
- It avoids the cumulative effects of fossil carbon exploitation.
- CO_2 emissions are reduced or avoided.

Thus, C1 intermediates such as CO_2 become raw materials rather than pollutants. The success of CO_2 utilization technologies and their penetration in the market depends on developing processes that can be feasibly scaled to an industrial level. It is also essential that any new CO_2 utilization process have a lower carbon footprint over its total supply chain than equivalent products manufactured from fossil resources. In this regard, microbial CO_2 utilization holds much promise. Photoautotrophic microbes such as algae and cyanobacteria use solar energy to capture carbon by photosynthesis, producing new biomass containing high quantities of protein, sugars, and lipids (see the sidebar "Photoautotrophic CO_2 Conversion by Microalgae"). These organisms can produce much more biomass per hectare than terrestrial crops, using nonarable land with closed nutrient cycles. Thus, compared with fuel crops, microbiological approaches do not compete with food production. Chemolithotrophic microorganisms (see the sidebar "Chemolithotrophic CO_2 Conversion by Gas Fermentation") can convert C1 intermediates (e.g., CO_2, CO, and formate) sourced directly from industrial streams, so additional capture technologies for purification or concentration are not needed. In this way, chemolithotrophs can transform carbon pollution into useful products such as ethanol or acetate, or additional value can be added by bioconversion to lipids using yeast. Chemolithotrophic microbes can prevent CO_2 emissions by using chemical energy sourced from waste streams. Examples are carbon monoxide from steel production, hydrogen from syngas, sulfur from petroleum refining, and minerals from mining waste. Alternatively, hydrogen can be produced via electrolysis using renewable electricity, which would allow almost unlimited expansion if the price of electricity continues to decline.

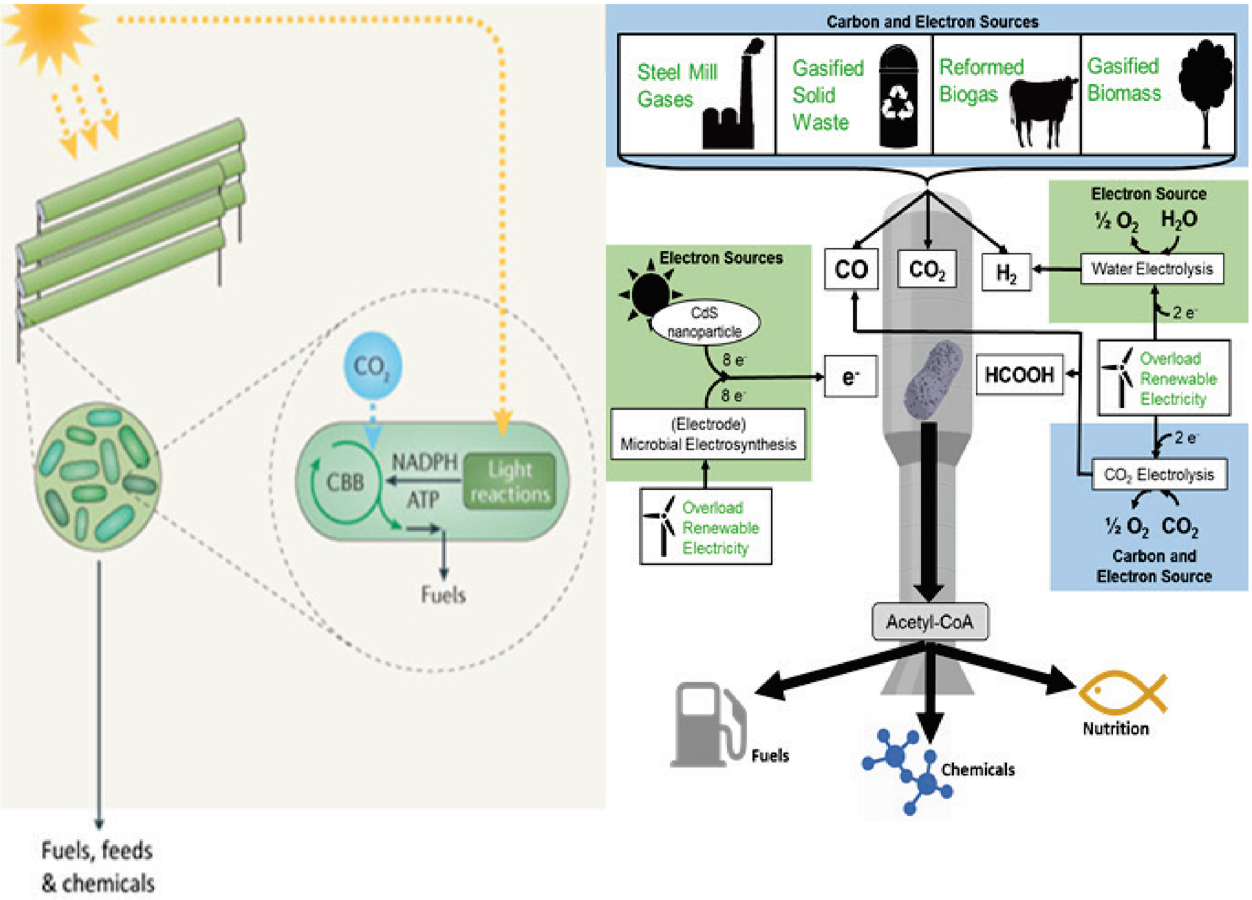


Figure 3.16. Examples of CO_2 conversion by photoautotrophic (left) and chemolithotrophic microbes (right). | Left: Reprinted by permission from Nature Publishing Group: *Nature* **14**, Fuelling the future: Microbial engineering for the production of sustainable biofuels, J. C. Liao, et al., 288–304. Copyright 2016. Right: Modified from Liew et. al. 2016. Gas fermentation: A flexible platform for commercial-scale production of low-carbon fuels and chemicals from waste and renewable feedstocks, *Front. Microbiol.* May 11. Used under the terms and conditions of the Creative Commons Public License.

Photoautotrophic CO_2 Conversion by Microalgae

Photoautotrophic microorganisms such as microalgae use photosynthesis to convert CO_2 into biomass with sunlight. They include a diverse range of organisms found in all aquatic environments, including the oceans, freshwater lakes, and highly alkaline ponds. They typically grow as free-floating cells but can also form dense microbial mats. They take CO_2 and nutrients such as ammonia and phosphate from the water. The cells are rich in proteins that can be used as feed. They can also be induced to accumulate triacylglyceride oils. Biomass can be converted to products via approaches like hydrothermal liquefaction, extraction of oils, or complete biorefinery concepts.

Mass cultivation of the microbes can be achieved in large outdoor growth systems by providing sufficient nutrients, which usually limit growth in the natural environment. The growth systems can be natural lagoons, shallow constructed raceway ponds, or enclosed photobioreactors. Diffusion of CO_2 from the atmosphere is not sufficient to maintain dense and productive cultures. To avoid CO_2 limitation and maximize productivity and solar efficiency, CO_2 is provided to the cultures, typically by sparging with a CO_2-enriched gas, for example, flue gas.

Large-scale cultivation of photoautotrophic microorganisms has key advantages over terrestrial plant crops. They can produce considerably more biomass per unit land area, can utilize land not suitable for traditional agriculture, can make use of brackish and saline water, and can fully utilize nutrients, avoiding cumulative effects from runoff. However, there are challenges in cultivating photoautotrophic microbes cost effectively. In outdoor environments, productivity can be compromised by fluctuating temperatures and light, and by invasion of exogenous organisms.

Image courtesy of Delhi Wastewater Treatment Plant

Chemolithotrophic CO_2 Conversion via Gas Fermentation

Gas fermentation makes use of microorganisms known as acetogens. These convert CO_2 and other C1 molecules such as carbon monoxide into fuel, chemical, and nutrient products. Gas fermentation processes can thus utilize a wide range of feedstocks including gasified organic matter of any sort (e.g., municipal solid waste, industrial waste, biomass, and agricultural waste residues) or industrial waste gases (e.g., from steel making, oil refining, or the ferroalloy industry). In this way gas fermentation can act as a vital bridge in the effort to create sustainable value from waste and enable the perpetual capture of greenhouse carbon in valuable materials.

Commercial gas fermentation processes are now being pioneered using industrially robust microbial strains and specialized bioreactor designs for the continuous production of low-carbon-transport fuel from industrial waste gas streams. Gas fermenting microbes use the highly efficient one-carbon Wood-Ljungdahl pathway to harness the carbon and energy in mixtures of CO, or CO_2/H_2, or CO, CO_2, and H_2 gases for both microbial growth and the synthesis of fuels (such as ethanol) and chemicals, such as 2,3-butanediol. Converting gases to fuels has been traditionally achieved via thermo-catalytic processes at high temperature (150–350 °C), and pressure (>30 atm) reactions (De Klerk et al., 2013). Gas fermentation offers numerous advantages over these chemical processes as it takes place at ambient temperatures and low pressures, which allows significant energy and cost savings while achieving greater selectivity to the target product.

A gas fermentation facility at the Shougang Steel mill in Caofeidian, China. Commercial-scale biological gas fermentation processes are currently being deployed to convert carbon-rich gas waste streams produced through steel manufacturing into low-carbon fuels. Pioneer plants are able to produce over 45,000 tonnes of fuel per annum. | Image courtesy of LanzaTech Inc.

3.4.1 Status of Biological CO_2 Utilization

There is an opportunity to develop industrial bioconversion of CO_2 by building on a long history of fundamental and applied investigation. For bioprocessing, the rise of industrial biotechnology has established methods for large-scale microbial cultivation and product recovery. More recently, this knowledge has been applied directly to CO_2 by utilizing microbes like acetogens and microalgae to make advances such as

- Improved biomass processing operations, including cell rupture, lipid extraction, biomass conversion, cell harvesting

- Design and large-scale demonstration of cultivation systems
- Life-cycle analysis and technoeconomic assessment of large-scale cultivation processes

In relation to the underlying biology, traditional methods of isolation and cultivation have determined phylogenetic relationships, developed knowledge of basic physiology and metabolism, and helped establish extensive culture collections. However, tapping into the immense biodiversity of carbon-utilizing organisms, has only just begun. Recently there have been unprecedented advances in biology that could empower new directions for CO_2 conversion. For example, bioprospecting for new strains can now be accelerated through the application of *ultra-fast and cheap DNA sequencing.* These capabilities also allow identification of new organisms, genetic changes in mutants, evolved organisms and unravelling of complete microbial consortia. These can now be characterized and understood at the genetic level. *Metagenomics* now gives the ability to identify and quantify the capabilities and actual conversions of individual species within mixed microbial communities. This computationally intensive approach depends on DNA sequencing, RNA sequencing, proteomics and metabolomics. This enables us to determine complex ecological interactions within "microbiomes" in more detail than ever before. Few if any systematic metabolomics studies have been performed to investigate inter-species and algal-bacteria interactions. Similarly, studies of the dynamics of consortia of chemolithotrophic microbes are currently lacking.

There has been much recent technological progress in molecular biological tools that could help expand the range of microbes and their capabilities. *"Omics" technologies and systems biology* mean that for the first time we can quantify and model conversions of biomolecules in cells, providing a holistic view of cellular physiology. This approach can provide an integrated view of cellular functions, constructed from cell-wide measurements. This includes regulatory networks, signal transduction, metabolism and energetics, among others. *Genome-scale and cell-wide models* can be developed that capitalize on inputs provided by cell-wide data. While there is some knowledge of the cell physiology, metabolism (Figure 3.17), and physiochemical properties of selected commercially interesting photoautotrophic microbes (e.g., *Nannochloropsis*, *Dunaliella*, *Haematococcus*, and *Chlorella*), detailed systems biology is yet to be fully applied to these organisms. The promise of omics technologies for photoautotrophic microbes has only just been recognized (Ryanet al. 2012), with some very recent advances (Jaeger et al. 2017).

Although metabolic engineering is a well-established field, there is a limited range of model microbes and metabolic pathways with which to work. This is particularly true with respect to C1 conversions. While the biology underpinning microbial growth on C1 intermediates is understood, the detail of the various mechanisms used by microbes to conserve the small amounts of energy available in these inputs for growth and product synthesis are poorly defined (Liew et. al 2016). Also, there are currently only a very limited number of CO_2 utilizing microbes for which genetic engineering can be performed. Gene sequencing and genetic modification have been established for some acetogenic Clostridia and for the microalgae *Chlamydomonas reinhardtii*. Beyond this, the genome of an industrial promising *Nannochloropsis gaditana* has recently been drafted (Radakovits et al. 2012), and genetic research on diatoms has commenced (Huang and Daboussi 2017).

There is now the possibility to apply *synthetic DNA* technology to the synthesis of new genes, codon optimized genes and whole pathways. This can accelerate pathway and microbe engineering and even the synthesis of entire organelles and functional cells is possible. There are also *powerful new technologies for editing genomes and pathways.* New methods such as CRISPRi and its derivatives provide efficient methods to modify microbial C1 metabolism. There is now an opportunity to apply these rapid modern methods to expand the range of C1 microbes and pathways to enable improved efficiency in CO_2 utilization (Banerjee et al. 2017). Genetic-engineering systems are now available for a small number of C1-utilizing strains (Liew et al 2016); however no examples exist of the high-throughput, automated, design-test-build-analyze platforms that are becoming the state of the art for strain improvement of

E. coli. While it is currently possible to produce ethanol from a range of substrates via gas fermentation, or isobutyric acid from CO_2 powered by iron oxidation, a major advance would be to enable the production of a more diverse range of chemically reduced products.

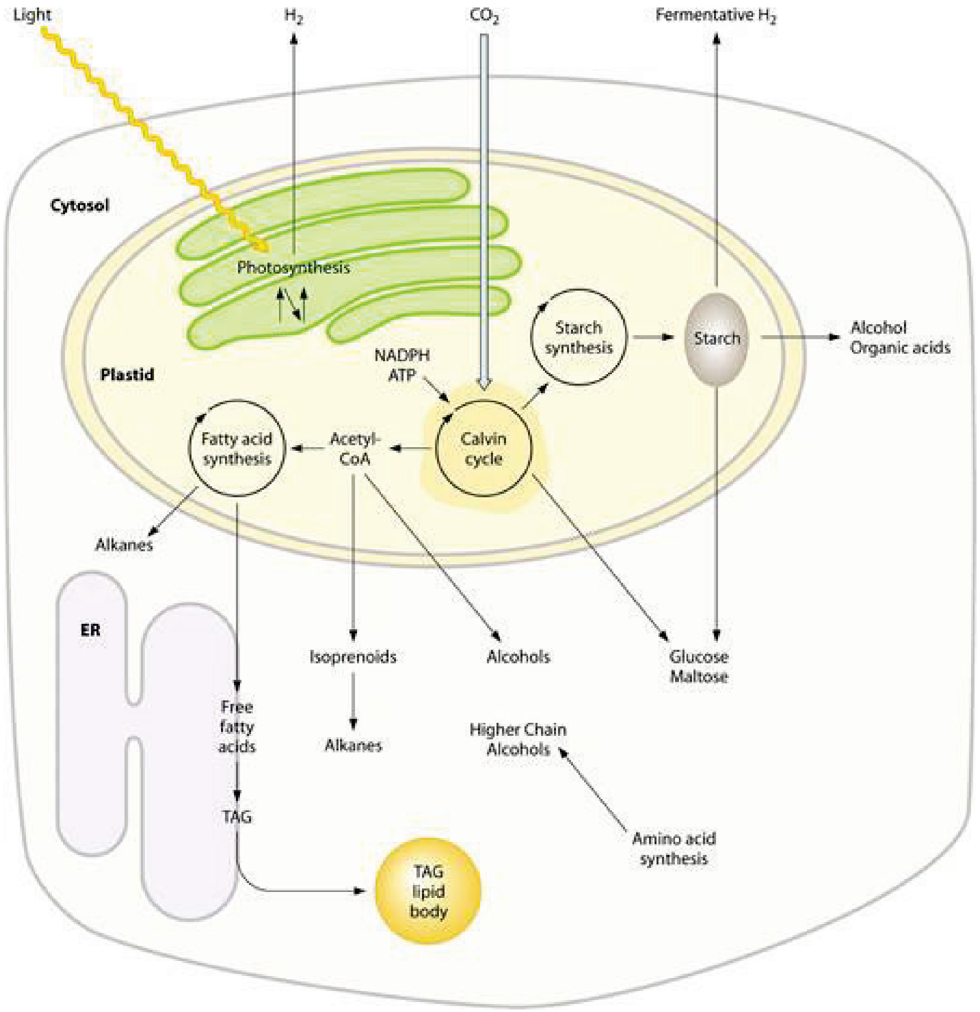


Figure 3.17. Metabolic pathways in photoautotrophic organisms related to product formation. | Reprinted by permission from American Society for Microbiology, R. Radakovits et al. 2010. Genetic engineering of algae for enhanced biofuel production. *Eukaryotic Cell* **9**(4), 486–501, copyright 2010

The current level of scientific and technical knowledge has spurred the establishment of a number of commercial facilities, e.g., the use of Clostridia for conversion of waste gases to ethanol [Bullis 2010]and production of high-value, low-volume products from microalgae (e.g., pigments and specialist nutritional products). As such, the overall amount of CO_2 utilized by microorganisms in industrial facilities today is not globally significant. To move beyond this level, new science is required to dramatically reduce costs by improving process rates and robustness.

3.4.2 Scientific Challenges

Two main challenges must be overcome to increase the impact of microbial CO_2 utilization–increasing productivity and expand the portfolio of products.

1. Increased productivity (intensification) to reduce costs

   While the current commercial facilities demonstrate the technical feasibility of microbial carbon utilization, the technologies must be deployed more widely and at much larger scale to have a significant impact on carbon dioxide sequestration. To achieve this scale, the productivity of microbial CO_2 conversion must be increased to reduce costs. This is required for large-scale production of high-volume products to be economically competitive. For photoautotrophic organisms productivity is measured on an areal basis (i.e., mass of product per unit land area per unit time), related to the usage of the available land and incident sunlight. This is the most important parameter for profitability of these applications (Davis et al. 2016). For chemolithotrophic organisms, productivity is volumetric (product per unit reactor volume per unit time). Increased productivity will both decrease capital expenses and reduce operating costs.

2. A broader range of products to expand markets and increase impact

   To significantly impact atmospheric carbon levels, the product portfolio of biological CO_2 conversion must also be expanded to access the high-volume product markets of fuels, feeds and chemicals. While chemolithotrophs can produce ethanol in industrial scale gas fermentation (see the sidebar "Chemolithotrophic CO_2 Conversion via Gas Fermentation") and phototrophs (oleaginous strains) can accumulate a large fraction of lipids, the manufacture other products has yet to be demonstrated at scale. Using C1 feedstocks as the basis for the production of platform chemicals is a new challenge in applied biology. An additional challenge for all CO_2-utilizing microbial systems is to maximize the value of co-products (like proteins, lipid or carbohydrates). All these carbon fixing organisms are cultured as dilute suspensions. Efficient recovery of products from water is a challenge for which bio-inspired solutions can be sought.

There are a range of research directions that can help overcome these fundamental challenges. Scientifically, researchers need to develop a sufficient understanding of the C1 microbes, metabolism, and consortia to underpin the following advances: (1) enhanced microbial metabolism, (2) increased gas-to-liquid mass transfer, (3) more robust microbial cultures or consortia, and (4) ability to produce an expanded range of products.

A key scientific challenge is to improve the productivity of the microorganisms or consortia that have inherent energetic challenges and a high degree of systems-based complexity. These organisms convert CO_2 (an energy-intensive process) using limited and fluctuating resources, possibly in open systems. As such these processes are challenging to intensify and can be susceptible to culture failure. Maximizing the efficiency of one carbon metabolism in these organisms is a major scientific challenge in systems and/or synthetic biology.

In addition to developing a better understanding of existing model organisms, it would be advantageous to establish more effective pipelines for bioprospecting of novel organisms, suited to industrial application. These organisms and their associated metabolic pathways could be integrated with the capabilities of established microbes. To facilitate this integration, effective high-throughput screens need to be developed that will assess the ability of isolates or mutants not to simply accumulate more product but do so at higher efficiency and yield.

Many microbial CO_2-utilization systems involve consortia of organisms (deliberately or inadvertently). There is a need to understand the microbial dynamics and interactions to make systems that are more robust. This requires detailed scientific investigations into the ecological interactions in the context of environmental or process dynamics.

Microbes can funnel carbon into value-added chemicals via defined pathways allowing high-yield production of a single desired product. If biological conversions could be coupled to chemical catalysis, the range of products that can be produced could be expanded tremendously. One example is an alcohol-to-biojet fuel process, in which alcohol is produced via gas fermentation and then chemically converted to biojet. There are numerous similar possibilities whereby catalytic and biological systems can be combined in any order to benefit from the best attributes of each technology while expanding the range of products that can be synthesized.

Microbial cultures for CO_2 utilization are dilute suspensions. Removing water can be a multistage process involving surface chemistry (e.g., coagulation and flocculation), rheology (e.g., dewatering) and process engineering. The effects of upstream biology on these processes are still not fully understood. Continued improvement of our understanding of the interactions between growth conditions, cell physiology, and harvesting/dewatering processes, will be important to reduce costs. To this end, processes will have to be so designed for easy product separation that does not require removal of vast amounts of water. Such possibilities would include systems producing gaseous products (e.g., methane) or products that are sequestered in the growth medium, such as intracellular polymers or lipids. Water use and biomass separation costs may also be minimized by cultivating phototrophs in attached biofilm bioreactors (Podola et al. 2017). Once the products have been recovered, it is important to put the process water to the most beneficial use. Continued investigation should be made into the effect of water recycle on culture performance and minimizing net water consumption.

Life cycle analyses and technoeconomic assessments are critical in guiding scientific research, policy, and commercial endeavors. These studies should continue to be refined and updated, particularly as new science and technology are developed.

3.4.3 Why Now?

To unlock the enormous potential of biological carbon utilization for product synthesis, groundbreaking science is needed. A number of recent advances will allow a new thrust in research to make transformative changes. In particular, systems and synthetic biology, machine learning, and computational power have all improved dramatically in the past few years. These tools will allow rapid development of fundamental scientific understanding to support technological breakthroughs that will reduce costs and accelerate the implementation of industrial production of feeds, fuels and chemicals. Modern biological tools are yet to be employed in full force on these systems. With the increasing pressures to act on reducing atmospheric carbon, now is the time to take full advantages of scientific advances to accelerate the implementation of microbial CO_2 utilization.

3.4.4 Conclusions

Microbial CO_2 utilization has the potential to shift the way we view CO_2 . If increasingly affordable technologies can be developed through the application of scientific advances, it will contribute to the establishment of a new industry that values carbon-rich emissions, encouraging investments in innovation and reducing CO_2 emitted to the atmosphere.

- Improved robustness enables the scaling of industrial microbial carbon fixation. Easy, relatively low cost access to (concentrated) carbon dioxide can prove to be a factor of significance in developing CO_2 utilization activities. The availability of CO_2 by itself will incentivize businesses to start looking for possible opportunities.
- Increasing gas–liquid mass transfer rates would enable the utilization of low-concentration gas streams. It may even enable sufficiently productive photoautotrophic growth to occur via the transfer of atmospheric CO_2 into the culture medium. This would decouple biomass production from point sources of CO_2, greatly expanding the number of viable cultivation sites and the amount of CO_2 that can be utilized directly from the atmosphere.
- Therefore, research that increases the robustness of microbial carbon conversions will significantly advance scale-up of the technology to the industrial commercial scale. Basic research will unlock the potential for synthesizing chemicals and fuels from CO_2. Hybrid catalytic-biological processes will increase the versatility of precursors and products.

3.5 Utilization Panel Report: Enhanced Unconventional Hydrocarbon Recovery with Carbon Storage

The technology of using CO_2 for enhanced oil recovery (EOR) from conventional reservoirs is a well-established method of CO_2 utilization and has been in place for more than 30 years. Unfortunately, natural CO_2 is often mined and used for EOR. Thus, the net environmental benefit of CO_2 utilization for EOR has been debated and the captured anthropogenic CO_2 is being phased in.

Over the past decade, the advancement of horizontal drilling, hydraulic fracturing and water flooding technologies has transformed energy recovery, particularly in the United States, and allowed the development of unconventional resources such as shale gas and tight oil. *However, the extensive use of water for energy recovery is environmentally unsustainable in the long term, and a large fraction of these resources in the world exist in places where water is scarce, including China.* Therefore, the use of alternative working fluids such as CO_2 has been proposed for enhanced hydrocarbon recovery. The use of CO_2 injection in unconventional and conventional reservoirs has the dual benefits of enhancing hydrocarbon recovery and storing CO_2. Large-scale CO_2 storage following the hydrocarbon recovery stage has been proposed and investigated at various locations.

One of the challenges of injecting CO_2 into geologic formations with low permeability is the formation of fractures. *Thus, the understanding of natural and engineered fractures in "nanoporous" media associated with both energy recovery and the subsequent carbon storage is important. The CO_2-mineral-water interactions can vary significantly depending on the mineralogy and water chemistry within each reservoir, resulting in altered fluid transport behaviors* (Figure 3.18). Unlike carbon storage in deep saline formations or storage associated with EOR in conventional reservoirs, enhanced unconventional hydrocarbon recovery using CO_2 is still an unknown technology. Thus, advanced scientific understanding of CO_2 reactivity and interactions in natural pore spaces, and between fracture and matrix components of rocks with multiple permeability levels, is essential for using CO_2 as a working fluid in tight reservoirs with the potential for storage.

3.5.1 Scientific Challenges

Several fundamental challenges exist in using CO_2 for enhanced hydrocarbon recovery, including (but not limited to) a lack of fundamental understanding of fluid flow in low-permeability (i.e., nano-Darcy environment) regions, the behaviors of natural and engineered tracers determining fluid migration, and reactive and interfacial phenomena of CO_2 in heterogeneous pore networks in rocks with varied chemical composition. To better understand the fate of the fluid injected into geologic formations with low permeability, fundamental studies at the molecular scale and mesoscale with field-scale investigations should be combined.

3.5.2 Research Directions

To accelerate the fundamental understanding of CO_2–reservoir interactions and their chemical and physical changes throughout energy extraction operations, there should be consistent protocols for experimental and modeling studies [Gadikota, Swanson, Zhao, and Park 2014), in-depth characterizations of unconventional hydrocarbon reservoirs, and well-designed field studies. Although some of the challenges with using CO_2 for enhanced hydrocarbon recovery are unique—such as low permeability and chemo-morphological heterogeneity of the reservoirs—it is now possible to transfer understanding of geologic CO_2 storage and enhanced hydrocarbon recovery from conventional reservoirs to accelerate the use of CO_2 for enhanced hydrocarbon recovery. Further, the development of several in-operando synchrotron and neutron scattering, tomography, and spectroscopy techniques has enabled a fundamental understanding of CO_2-heterogeneous surface interactions at multiple length scales. Specialized laboratory-scale instrumentation, such as high-pressure fluid displacement pumps and custom-designed reactor systems, have been developed to mimic in situ geologic environments. At the field scale, the development of advanced well-diagnostic tools for various geological applications, including the detection of natural gas hydrates, is now transferable for accelerating the use of CO_2 as a working fluid in extreme environments. Novel synthetic materials can also be used to provide insights into these highly heterogenous geologic materials. As CO_2 interacts with rocks like shale in the presence of groundwater, some have reported that there is significant growth of interesting pore networks leading to increased permeability. The rock–CO_2 interaction can also lead to leaching of heavy metals and radioactive materials into the fluid phase. Thus, the fate of various rock components during CO_2 injection and subsequent storage in shale formation should be investigated to comprehensively estimate the net CO_2 reduction and environmental impacts.

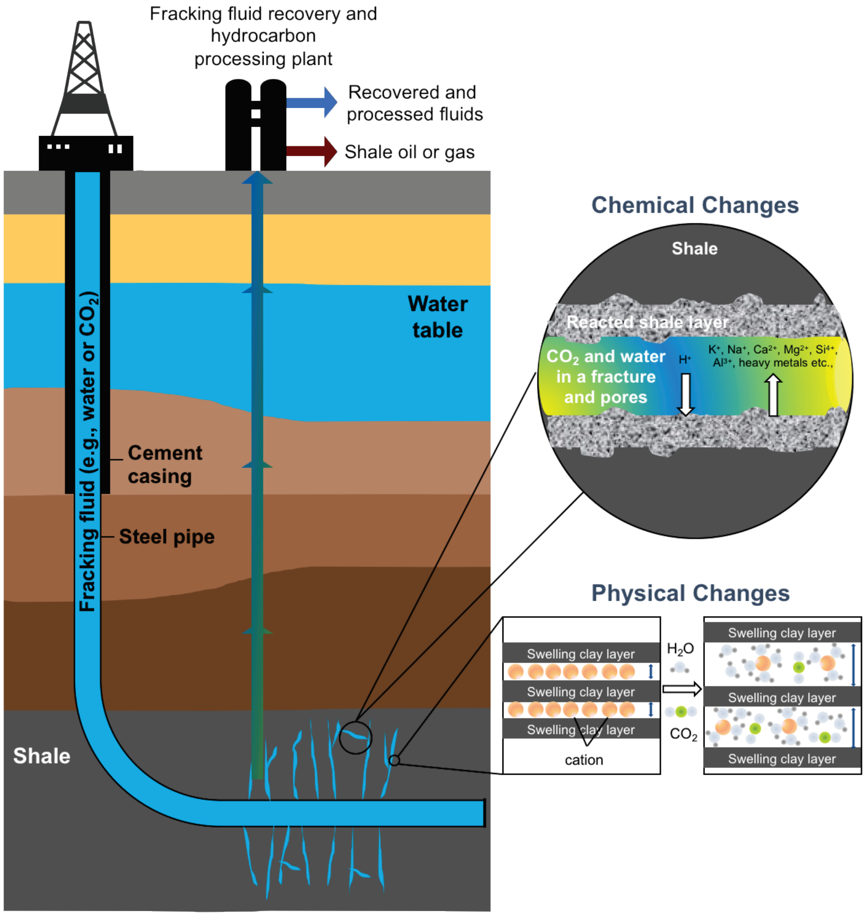


Figure 3.18. Potential chemical and physical interactions between CO_2 and shale when CO_2 is employed as an alternative hydrofracturing fluid.

3.5.3 Conclusions

A fundamental physical and chemical understanding of CO_2–water–solid interactions in extreme environments and in confined regions of variable geometry from the molecular to the field scales is essential for the effective utilization of CO_2 as a working fluid (e.g., fracking fluid) in a wide range of geologic environments. The use of CO_2 in energy recovery is important for unlocking the potential for both conventional and unconventional hydrocarbon resources while improving overall sustainability, including net carbon emission and water requirements. Accelerated innovations in this area are possible through advanced materials discovery to tune materials chemistry in complex environments, the development of well-defined protocols for controlled laboratory- and field-scale measurements, and dynamic optimization of the fate of a fluid containing various components originating in rocks and CO_2 based on dynamic upscaling and downscaling studies.

3.6 Carbon Dioxide Utilization Priority Research Directions

3.6.1 PRD U-1: Valorizing CO_2 by Breakthrough Catalytic Transformations into Fuels and Chemicals

Using CO_2 as a carbon source to create value-added compounds from waste emissions streams is a critical component of any CCUS strategy. In addition, this approach would present an alternative to producing fuels and chemicals from fossil feedstocks such as gas, oil, and coal. There are numerous technical challenges in CO_2 conversion, however: CO_2 is highly stable, oxygen rich, and often present in impure streams. Current catalytic technologies optimized to convert oxygen-poor feedstocks to produce fuels and chemicals cannot be applied to CO_2, and there is a lack of methodologies for CO_2 conversion. However, breakthrough catalytic transformations enable the valorization of CO_2 streams in a selective and energy-efficient manner, resulting in new production routes to both established and new products.

Scientific Challenges

Fossil fuels meet 85% of the world's energy needs and represent the largest source of anthropogenic CO_2 emissions. Petrochemicals are the basis for over 95% of organic chemicals, such as plastics, insecticides, drugs, and fertilizers. Their dominance is the result of over 100 years of catalytic sciences research in the transformation of fossil resources, with an economic impact reaching between 30 and 40% of the global gross domestic product. In contrast, CO_2 is currently not being exploited to its full potential as a carbon source because of its stability, with less than 300 Mt of CO_2 being transformed per year. However, the use of CO_2 as a carbon source opens new avenues for sustainable production and is an economic driver to support CCUS.

Carbon dioxide is a chemically stable compound. Energy must be supplied to break a carbon-oxygen double bond (C=O) or change it to a carbon-oxygen single bond (C-O) and therefore transform CO_2 into valuable products. This change can be achieved in several ways that involve heat, pressure, a high-energy reactant, electromagnetic radiation, or a combination of these. To reduce the overall energy requirement, a catalyst is employed in the majority of thermochemical and hydrogenation reactions of CO_2.

Using CO_2 streams requires a new approach to catalysis to promote the transformation of a new and unique feedstock, CO_2, in a selective and energy-efficient way. Such a source shift poses new scientific questions: How can we transform CO_2 into established products and new ones that have never been made from CO_2? How can we utilize CO_2 streams of varying compositions, including dilute CO_2 concentrations, high water levels, and additional impurities that may act as catalyst poisons?

Research Directions

Groundbreaking catalytic systems are needed to convert CO_2 in an efficient, selective manner. This PRD focuses on four specific research directions:

1. Discover new catalysts for selective chemical bond formation involving CO_2.
2. Use advanced computational and in situ characterization techniques to elucidate reaction pathways and catalytic mechanisms.
3. Investigate multifunctional catalysts for tandem CO_2 capture and conversion to fuels and chemicals under energy-efficient conditions.
4. Devise intensified processes that exhibit robustness and energy efficiency using various CO_2 streams.

Selectivity is a common issue in catalysis, and it is particularly challenging in CO_2 conversion because of the stability of the CO_2 molecule. Catalytic systems must be designed to activate and transform the stable C-O bonds in CO_2 and unveil new reaction pathways for the selective formation of C-H, C-C, and C-heteroatom bonds. This effort could include, for example, the discovery of solid, nanostructured, and/or molecular catalysts. Combining faster catalysts with advances in reactor design and process engineering could circumvent the low thermodynamically limited product yields in some reactions.

Mechanistic investigations of CO_2 activation and catalytic pathways are essential to providing the rational and efficient design of catalysts and helping discover new transformations. Advanced computational and in situ characterization techniques are invaluable tools in this effort. Mechanisms and kinetics must be evaluated, for example, to determine the optimum conditions under which to achieve close-to-monodispersed fractions in synthetic fuels production. This research needs to be carried out in tandem with catalyst development. In an ideal case, a single reactor could in theory be dynamically tuned to produce gasoline fractions under one set of conditions, kerosene under a second, and diesel under a third; but reaction pathways and catalytic mechanisms must first be elucidated at the fundamental level before this can be applied.

Exploring and expanding multifunctional catalysts capable of tandem CO_2 capture and conversion represent an opportunity for optimal energy efficiency in the production of fuels and chemicals. Currently, processes are dependent on a pure CO_2 stream, and it is assumed that flue gases must be purified before they can be used. This is contrary to the notion that chemical adsorption of CO_2, as is true in the case of amines, should be used in carbon capture. The reaction of CO_2 with, for example, monoethanolamine produces a new chemical that is then destroyed to regenerate the amine and pure CO_2. What if the capture agent were instead a co-reactant that led to a value-added product in itself. This would improve potential process economics and would be a chemically and environmentally sound way of solving the capture-conversion problem. Even better would be the notion that the product interactions with the catalyst changed so that it spontaneously desorbed under reaction conditions.

Carbon dioxide streams are diverse by nature. They are by-products of industrial processes generated upon the decomposition of biomass and also found in the atmosphere. To enable the transformation of these streams directly, catalytic systems must be robust and able to convert CO_2 despite varying conditions, purity levels, water levels, and CO_2 concentrations. To enable widespread CO_2 conversion, energy-efficient and intensified processes must be discovered to achieve cost-effectiveness and reduce life-cycle impacts. Energy efficiency is the first criterion in CO_2 conversion to fuels, as the reduction of CO_2 is, by nature, energy-intensive. In this respect, suitable reductants, such as dihydrogen derived from renewable sources, must be used. Catalysts should be earth-abundant, or they should be readily recoverable post-reaction without increasing the economic or environmental burden.

Technology Impacts

Advancing catalytic sciences applied to CO_2 conversion will foster dramatic advances in the scientific community and in the development of CCUS. Such research would specifically enable the following:

- Development of impurity-tolerant catalysts and multifunctional catalysts
- Advanced catalytic strategies for the reduction of C-O bonds, applicable beyond CO_2 to the conversion of other renewable carbon sources (e.g., biomass, waste chemicals)
- Rational design of CO_2 reaction pathways on catalyst sites, through simulation and mechanistic understanding

Significant advancements in CO_2 valorization would benefit not only the greater scientific community but also the CCUS sector by

- Adding value to CCUS with new and alternative carbon-based feedstocks for industry and reducing CO_2 by both utilization and avoidance
- Using flue gas with purification and concentration built into the product formation step, thereby reducing the cost and environmental burden of a separate isolation step
- Removing new fossil carbon entering the supply chain by using CO_2 as a C-1 building block

- Sequestering some CO_2 into chemical products, some cycled through fuels, which would help in the development of an accelerated carbon cycle

Conclusions

Carbon dioxide is a key feedstock and offers a new opportunity in the production of fuels and chemicals. This opportunity is as rewarding as it is challenging in terms of catalysis science and breakthrough catalytic strategies, and systems must be designed to reach the potential of CO_2 utilization in value-added products. One major bottleneck is the financial and energy penalty incurred in capturing and purifying CO_2 before its utilization in C1 chemistry. This can be addressed by building the capture step into product formation, with catalysts chosen that can withstand the presence of other impurities consistent with waste gas streams. Fundamental catalyst development should always keep in mind the 12 Principles of Green Chemistry and should strive to use abundant or readily recycled and reprocessable metals in their design. Because of the vast quantities of CO_2 that need to be processed, highly intensified, continuous-flow reactors will probably be needed; that requirement puts an additional burden on the design of catalysts, as they must be able to operate in fixed- or fluidized-bed environments. Likewise, reactors need to be adaptable to accommodate not only thermochemical reactions but also hybrid reactions involving photocatalysis and/or electrocatalysis. The conundrum here is that homogeneous catalysts, often associated with batch processes, offer degrees of selectivity not observed in heterogeneous systems, which are more readily able to process reactions in flow systems. Therefore, catalysts may need to be developed that can combine the properties of both, perhaps with some degree of compromise [Phan et al. 2004].

3.6.2 PRD U-2: Creating New Routes to Carbon-based Functional Materials from CO_2

Carbon-based materials (e.g., polymers, carbon fibers, composites) are extremely versatile advanced products that have a wide and rapidly expanding range of high-value applications; they are highly desirable owing to their superior performance over traditional materials. However, their production is currently reliant on fossil sources. Current production has a high emissions footprint, and in some cases (e.g., carbon fibers), feedstock availability, production capacity, and cost are limiting application on a much larger scale.

Fundamental research on novel routes to synthesize these materials from a CO_2 feedstock is timely and desirable. This approach has the potential to reduce emissions, both directly (from synthesis) and indirectly (from usage), while simultaneously expanding both the volume and range of carbon-based functional materials available. Unlike the manufacture of fine chemicals, production of carbon-based materials from CO_2 would not result in market saturation. Rather, it would allow for a dramatic expansion of existing applications, with an associated substitution of existing materials for new materials that exhibit superior properties.

Scientific Challenges

Development of methodologies to produce key structural and/or functional carbon-based materials directly from CO_2 has the potential to reduce overall process emissions and environmental impact while simultaneously allowing for increased deployment of these materials. Furthermore, there are opportunities to develop processes that avoid the use of toxic or environmentally questionable reagents. New production methods may also offer novel opportunities for the control of material structure, morphology, and composition. This will allow for the tailoring of the materials properties, potentially opening them up for an even wider range of applications.

Many advanced materials contain aromatic groups to impart properties such as high strength (e.g., Kevlar), electrical conduction (e.g., graphene and polythiophenes) and electro-optic response (e.g., LEDs and organic LEDs). Carbon dioxide utilization in the production of aromatics, and particularly heteroaromatics, is particularly challenging but should be regarded as a key target within this theme.

A growing area of importance is high-strength, low-weight materials for vehicle construction, particularly in aerospace and automotive applications. Carbon fibers have made a great impact in this respect as components of polymer composites. Carbon fibers are traditionally formed from polyacrylonitrile (PAN) filaments that are anaerobically decomposed to assemble carbon structures. PAN–carbon fiber production is limited by the synthesis of the PAN, which has less than favorable environmental credentials. Furthermore, demand is currently much higher than supply. Recent studies by Licht and co-workers [Ren et al. 2015] have suggested that carbon nanofibers (CNFs) can be produced directly from CO_2 using electrochemical means. Bulk carbon fibers can be incorporated into a number of composites based on organic polymers and even metals. Carbon-reinforced plastics have been used in high-performance sports equipment and sports cars for many years. Carbon fiber–reinforced aluminum is used in the fuel tank of the Hyundai i35 hydrogen fuel cell vehicle. However, CNFs are now making impacts in more consumer-driven applications. CNFs have a number of unique properties, including high tensile strength and enhanced electrical conduction. The properties are enhanced when the individual fibers aggregate to form larger bundles, rather than remaining isolated nanofibers.

Research Directions

One starting point for this research will be the synthesis of CO_2-containing precursors and/or monomers to impart properties that will allow for control of the structural and compositional evolution of materials during their production. Strategies for the utilization of CO_2 as a co-monomer in the synthesis of polymers with controlled molecular weights and distributions must be developed.

Approaches for directed synthesis of materials with controlled nano- and micro-structures from CO_2 must be explored, in particular, routes that avoid the toxic and polluting reagents and/or high-energy processes used in existing production methods.

Tandem development of catalysts and processes for increasing the yield and selectivity of a reaction between an alcohol or diol and CO_2 will accelerate the development of polymers with CO_2 integrated in the polymer backbone. Technology that addresses the low equilibrium yield and the removal of low concentrations of water at high temperature and pressure will open the door to a wide range of CO_2-containing polymers by increasing the range of available co-monomers. For example, biomass-derived diols or diamines could then be exploited to make polycarbonate or polyurea materials that are not currently accessible. Aromatic polycarbonates (as opposed to the aliphatic polycarbonates derived from CO_2 and epoxides), which are thermoplastic polymers with a range of applications, cannot yet be made from CO_2 but could also be accessible from CO_2 with this technology.

Carbon dioxide and alkenes can be coupled to make acrylic acid derivatives that can eventually be polymerized. Better catalysts and processes are needed, including better understanding of the chemistry so that propene (to methacrylic acid), and not just ethene (to acrylic acid), can be used. Larger-scale polymers, such as formaldehyde-based polymers, can be accessed if CO_2 can be efficiently reduced with two equivalents of H_2 to formaldehyde.

New and better catalysts are needed, including heterogeneous variants, for the copolymerization of CO_2 and epoxides into truly poly(aliphatic)carbonates. The goal should be improved control of chain length and distribution. Incorporation of other monomers into the polymer should be investigated to give the polymers improved properties for more applications. Polymer research into the blending and formulation of these polycarbonates is also needed to create a business case for their production.

A challenge for advanced carbon-based materials will be to produce carbon fibers and CNFs using thermal methods, in addition to electrochemical techniques. CNFs identified in Damascus steel are believed to give swords derived from this material exceptional strength and blade sharpness. The steel-making process was clearly thermal, so the evidence is there that incorporating CNFs is possible. One solution may be to use solar thermal energy, using heliostats and other solar concentrators to produce focused thermal energy to activate the process. The byproduct is pure oxygen, which can be collected and sold or used to fuel oxyfuel combustion processes. This is a good example of industrial symbiosis, in which oxyfuel combustion produces higher-purity CO_2, which in turn is pyrolized to CNFs and pure oxygen, which is then fed back into the process. This is an excellent example of a local accelerated carbon cycle. Thermal conversion from CO has been achieved using a $Ni/Fe(CO)_5$ catalyst; however, the challenge still remains to transform CO_2 directly [Nikolaev 2004].

Technology Impacts

Overall, this research will advance the understanding of controlled synthesis at the molecular level to produce materials with desired macroscopic properties. It should result in the development of new strategies and methods for tailored production of synthetic polymers with targeted functionality, molecular weight, and molecular weight distribution. This, in turn, will allow for the creation of innovative materials (e.g., novel carbon-based composites) with tailored properties.

Development of catalysts and processes that permit a wider range of co-monomers for polymerization with CO_2, especially diols, will likely have impact on other CO_2 reactions that require improved catalysts.

Because the materials targeted are expected have medium to long lives, expansion of their production using CO_2 as a feedstock will result in mid- to long-term sequestration of CO_2. The materials targeted are high–value-added products with a wide and growing number of application areas. In particular, structural carbon-based materials (e.g., carbon fiber and CNF composites) are highly desirable for use in transportation and construction applications. Indirect CO_2 emissions reduction will be realized as a result of substitution of carbon-based materials for traditional materials, such as steel and aluminum alloys, in construction and aircraft/vehicle design,. This can be achieved by using advanced materials that are lighter and exhibit properties superior to those of the materials they displace. The scale and emission levels associated with current production and use of materials for construction and transportation applications is such that widespread substitution with carbon-based materials could have a significant impact on global emissions and resource utilization.

Conclusions

Advanced materials with superior properties open new opportunities to reduce carbon impact while enhancing quality of life. Creating these materials from new CO_2 routes is low-TRL research providing opportunities to store CO_2 while enlarging market impact. Research is required now that seeks to develop a technology that will allow for production of materials, using CO_2 and renewable energy, that can be used on a large scale. The penetration of such materials into the market will have a dual impact on CO_2 mitigation. Covestro has already demonstrated a 9–20% reduction in CO_2 emissions for the CO_2-to-polyurethane-polyol process. A secondary mitigation benefit may be brought about by using high-strength, lightweight composite materials in vehicles, which will in turn reduce transportation emissions through increased fuel efficiency. Polymers, carbon fibers, and composites offer CO_2 utilization and mitigation potential while creating a circular economy through industrial symbiosis.

3.6.3 PRD U-3: Designing and Controlling Molecular-Scale Interactions for Electrochemical and Photochemical Conversion of CO_2

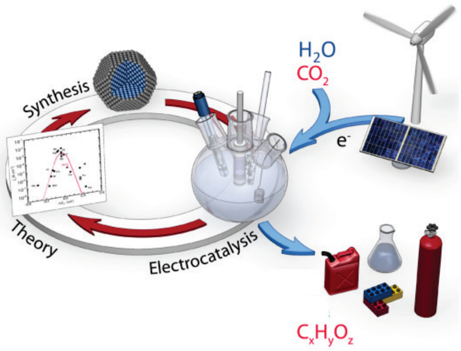


Figure 3.19. Renewable electricity (e.g. wind, solar) can be used to power electrolyzers that convert water and CO_2 into valuable carbon-based fuels, chemicals, and materials. | Adapted from Z.-W/ Seh et al. 2017. *Science* **355**(6321), eaad4998. Reprinted with permission from AAAS

If appropriate catalyst and photocatalyst systems can be developed, opportunities open up to transform CO_2 to carbon-based fuels, chemicals, and materials in an energy-efficient, low-temperature, sustainable manner (Figure 3.19). Designing and controlling molecular-scale interactions is crucial to achieving the performance needed. A major scientific gap must be surmounted to tailor electrochemical, photochemical and photoelectrochemical pathways, which often require multistep processes involving sequential, activated transfers of electrons and protons. With the appropriate design and synthesis of atomically precise, sophisticated catalyst systems, it may be possible to execute multistep, multifunctional, multiscale electron and proton transfers, akin to enzymes, while operating in a stable manner. Additionally, photochemical and photoelectrochemical approaches require stable light-harvesting materials with the required electronic structures, photovoltage, and charge separation. The successful development of selective, robust catalysts for CO_2 conversion can revolutionize the chemical, petroleum, and nutrient production industries.

Scientific Challenges

Current catalysts for CO_2 reduction are lacking; scientific needs and challenges in the area include the following:

- *Improved fundamental understanding of the sequential reactions* involving multistep, multi-electron, multi-proton transfers in CO_2 reduction. Elucidating mechanisms accelerates catalyst discovery.
- *Improved selectivity, energy efficiency, and stability*. An ideal catalyst would typically achieve 90+% selectivity for the desired product, at 90+% energy efficiency, operating for ~10^5–10^6 hours continuously; no current catalyst has these characteristics. Energy efficiency can be improved by lowering overpotentials on both the CO_2 reducing cathode and the oxygen evolving anode. Current photocatalysts as well as molecular electrocatalysts offer few pathways to >$2e^-$ products.
- *New photo-electrode materials that can meet all required properties*: appropriate electronic structure, high activity, stability, high voltage and charge collection efficiency, scalability (Figure 3.20). Current materials-based photocatalysts cannot simultaneously meet the requirements of electronic band structures and high stability. Molecular photocatalysts do not meet stability requirements.
- *Electrolytes with improved CO_2 solubility and diffusivity* to increase reaction rates. There is a need to improve knowledge of how pH and ions affect catalysis. For catalysts that operate in the gas phase, improved understanding of 2- and 3-phase boundary cooperativity could yield significant enhancements.
- *Understanding hybrid molecular/materials catalytic systems* that may realize challenging multi-electron multi-proton reaction pathways that are not accessible by either system individually, an approach that could pave the way to the design of low-cost catalytic systems.

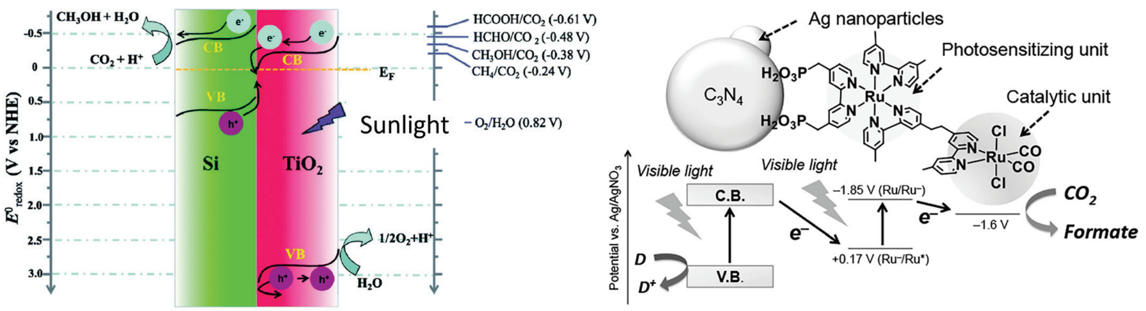


Figure 3.20. Photochemical conversion of CO_2 and H_2O to carbon-based products such as (left) methanol (CH_3OH) and (right) formate ($HCOO^-$). This process requires coupling photoabsorbing materials or molecules to catalysts, which often consist of either materials of molecular complexes. | (Left): Adapted from Y. Liu et al. 2014. *RSC Adv.* **4,** 56961–56969 with permission of the Royal Society of Chemistry. (Right): Image adapted from R. Kuriki et al. 2017. *Angew. Chem. Int. Ed.* **56,** 4867 by permission from John Wiley and Sons under the terms and conditions of the Creative Commons Attribution Non-Commercial License

Meeting these goals works toward developing atomically precise redox catalyst systems designed to follow precisely defined reaction mechanisms. Gaining fundamental understanding of reaction mechanisms allows us, through ab initio modeling and simulation, to predict performance. We can then develop and use methods to precisely control catalyst systems at the atomic level to maximize degeneracy among sites (for materials-based catalysts) that adhere to the desired mechanistic pathway(s).

Research Directions

The following research directions could revolutionize the development of CO_2 reduction catalyst systems:

- *Sophisticated catalyst systems* must be designed that can execute multifunctional, multistep, multiscale electron/proton transfers.
- *Multiscale theoretical and modeling tools* must be developed to elucidate key reaction phenomena.
- *New atom site–specific characterization methods*, in particular in situ/operando, must be developed that reveal energy, charge transfer, and excited state chemical dynamics, probing catalysts, interfaces, electrolyte gradients, reaction intermediates, cooperativity at multiple scales, degradation pathways, and so on.
- *Alternative oxidative chemistries* to water oxidation should be explored, along with new catalysts and other reactions.

Sophisticated catalyst systems and catalyst architectures

Developing future atomically/molecularly precise redox catalysts with the needed performance will require a deeper understanding of reaction mechanisms along with greater control in catalyst synthesis. The ability to make accurate ab initio predictions of catalyst systems followed by custom synthesis of the (photo)catalyst itself is a powerful combination. Conventional fabrication techniques often result in polydisperse particles and surfaces, nondegenerate reaction sites, and nondegenerate pathways. Single examples of atomically precise inorganic material systems have been demonstrated; however, they rely on nonscalable methods. Future synthetic strategies should be scalable and broadly applicable to a variety of possible promising catalysts, e.g., alloys, chalcogenides, and mixed-metal oxides.

Molecular electro- and photocatalyst structures should be finely tuned to match desired electronic and environmental effects at the metal active center. Combining one or several molecular catalysts with a heterogeneous material (e.g., in [nano]structured films or organized networks such as metal oxide frameworks, covalent organic frameworks, and polymers) may offer opportunities for achieving controlled cascade (sequential) transformations of CO_2. Immobilizing molecular catalysts on solid surfaces may also dramatically increase robustness and is well suited for mechanistic investigations. Control of elementary steps in the reaction is paramount.

Multiscale theoretical and modeling tools

A significant knowledge gap exists in linking structure-property-performance relationships for all CO_2 reduction catalysts, for material systems, and for molecular catalysts alike. Such knowledge could guide the synthesis of more active catalysts for a target reaction on a rational basis. The dynamic nature and complexity of catalyst structures and electrified interfaces make predictions challenging for new catalysts, a broad challenge in all of electrochemistry. The synergy between theory and experimental validation must be exploited with the development of new multiscale codes.

Characterization methods

The development and application of more advanced tools to evaluate catalyst performance in situ or operando could provide key knowledge needed to drive the field forward. Many difficulties exist in the collection and interpretation of complex signals that limit the application of most optical spectroscopies. X-ray techniques can be extremely useful, but the facilities and methods to perform true operando photoelectron spectroscopy with a liquid electrolyte are rare [Eilert et al. 2016]. There is tremendous opportunity to develop and improve methods. Understanding how catalysts restructure during operation, identifying the most active sites involved in the reaction, is a key goal,. Another is observing the molecular reactive intermediate species participating in the reaction). Measurements of local pH, ion concentrations, and solvent structure are also crucial to understand how they affect redox catalysis (Figure 3.21). Developing such characterization methods would provide valuable information directly to catalyst development efforts. For photochemical reactions, further gaps exist in fundamental understanding of charge dynamics and kinetics in photochemical CO_2 reduction that could also be addressed with in situ techniques. Better analytical techniques will hasten the discovery of efficient semiconductor photocatalysts/photoelectrodes.

There is also much to learn about degradation pathways of catalysts, through corrosion, poisoning or degradation of molecular structure. These deactivation processes need to be uncovered and remediation and/or regeneration strategies should be developed for CO_2 conversion technologies to emerge.

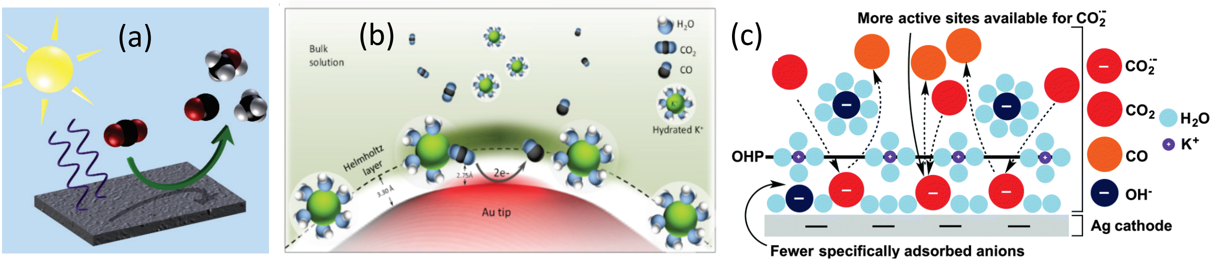


Figure 3.21. Controlling molecular-scale phenomena is the pathway toward effective photo- and electro-chemical conversion of CO_2 to fuels and chemicals. | (a) Reprinted with permission from J. L. White et al. 2015. *Chem. Rev.* **115**(23), 12888-12935. Copyright 2015 American Chemical Society. (b) Adapted from M. Liu et al. 2016. *Nature* **537**, 382–386, copyright 2016 American Chemical Society. (c) Reproduced from S. Verma et al. 2016. *Phys. Chem. Chem. Phys.* **18**, 7075-7084, with permission from the Royal Society of Chemistry

Alternative oxidative chemistries

A major impediment to high efficiency is the oxidation reaction; the anodic portion of the cell is often neglected in studies involving CO_2 electrolysis. For aqueous electrolytes operating at low temperatures, oxygen evolution requires a high overpotential, resulting in substantial energy losses; new catalysts for this reaction are needed. Alternatives to oxygen evolution or other simple oxidation reactions must also be explored and developed. Fortunately, other higher-value oxidation chemistries are possible, e.g. acetate, nitrate, sulfate, and other oxidized commodity products.

Technology Impacts

The research directions described, designing and controlling molecular-scale interactions for electrochemical and photochemical CO_2 conversion, have the potential to revolutionize the fuel and chemical industries. New processes can then be enabled that are inherently sustainable and capable of producing carbon-based products at a global scale using renewable energy and a cheap feedstock, waste CO_2, rather than sugars or fossil fuels. Capital expenses can be substantially reduced to allow for cost-effective processes. Deserts can become sustainable sources of fuels, chemicals, and perhaps even nutrients. Selective, on-demand, distributed chemical manufacturing could be achieved, opening up new markets and improving the quality of life for billions living in low-income communities. Sector coupling will enable the sustainable electrification of global industry.

Conclusions

There is a tremendous opportunity to establish the foundational scientific underpinnings involving molecular-scale phenomena in converting CO_2 to fuels and chemicals via electrochemical and photochemical pathways. Clear structure-property-performance relationships would enable the discovery of highly optimized redox catalysts with atomic precision that can be deployed at scale. Successful outcomes will include catalysts capable of using sunlight and/or electricity to convert CO_2 into >C2 products with >90% selectivity and >90% efficiency. Advances in this field will have a positive impact on a range of other industries as well, from batteries to pharmaceuticals to consumer electronics.

3.6.4 PRD U-4: Harnessing Multiscale Phenomena for High-Performance Electrochemical and Photochemical Transformation of CO_2

The development of high-performance electrochemical and photochemical systems that convert CO_2 into value-added products has the potential to transform an economy from one that depends on fossil resources into one that uses abundantly available CO_2 as a feedstock to produce fuels, chemicals, and materials. For these systems to become commercially viable, new system designs are needed that can operate under a wide range of conditions (e.g., variable power, impure reagents) to produce products efficiently and selectively. In addition to requiring robust catalysts of sufficient performance (see PRD 3.5.1), these systems need to be designed to facilitate effective transport processes, including those for electrons, ions, photons, and heat, as well as the reagent (CO_2, water) and product species. Development of this technology will also help advance related technologies for the storage of renewable electricity.

Catalyst development is crucial to enable heterogeneous, homogeneous, electrochemical, and photochemical processes that convert CO_2 into desired chemical products and intermediates used in large-scale chemical and materials manufacturing. Another pressing need is the design of cost-effective reactors for CO_2 conversion that efficiently deliver all the necessary components (e.g., reagents such as CO_2 and water; electrons/photons that drive the process) to the active sites of the catalyst while concurrently removing all reaction products and excess heat at a sufficient rate. Thus a major scientific challenge is how to control the transport of electrons, protons, electron-mediators, photons, ions, solvent, and reagents across multiple length scales. New, breakthrough designs for electrode/photo-electrode architectures are needed that facilitate multiscale processes to enhance the overall transport properties of the system.

A second scientific challenge is how to develop computational models capable of describing transport and reaction mechanisms across multiple scales. These models will require scalable and robust algorithms that can range from dynamics at the molecular scale that describe surface molecular reactions, all the way to macroscale transport behavior, chemical kinetics, and electric field descriptions, coupling all processes in between. *There is a significant opportunity to develop models that can effectively span many orders of magnitude across length and time scales*. Such a capability is required for robust simulation of the entire electrolytic system operating in a true reaction environment. The challenge is the coupling of nonlinear partial differential equations that describe these physical phenomena at different length and time scales with complex boundary conditions. Research is needed to develop computational methods that can perform such simulations in an accurate, robust, scalable manner.

Scientific Challenges

A third scientific challenge is system robustness. This challenge exists because the CO_2 reactors will likely operate with imperfect power feeds and impure component feeds, both of which can mitigate the performance and lifetime of the system. Design principles are needed to guide the integration of intermittent renewable electricity with a CO_2 electrolyzer system using low-grade CO_2 sources.

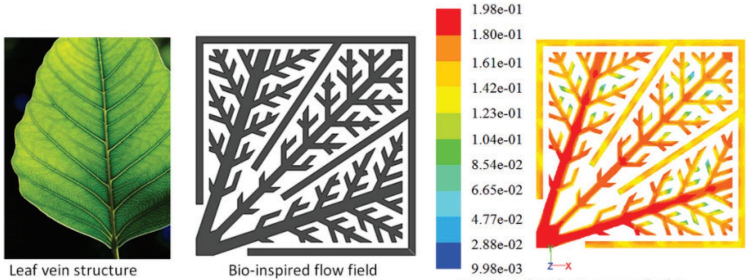
Research Directions

The following research directions are crucial to develop high-performance CO_2 conversion systems:

- *New architectures* for electrodes/photo-electrodes and flow field designs
- *Modeling tools and experimental methods* to understand three-phase systems, linking atomistic phenomena and macroscale transport
- *Integration:* combining CO_2 capture, conversion, product separation, reagent recycling
- *Cascading processes:* $CO_2 \rightarrow CO \rightarrow C_N$
- *Coupling* electro-photo-thermal-bio conversions

New architectures for electrodes/photo-electrodes and flow field designs

Electrochemical and photochemical processes involve physical and chemical processes occurring at multiple length and time scales that are intricately coupled with one another. Appropriate hierarchical structures can provide many benefits; e.g., increasing the surface area of (photo)catalysts for CO_2 conversion can improve activity by increasing the total number of active sites, potentially improving energy efficiencies (Figure 3.22). Highly porous electrocatalysts have also been demonstrated to show field-induced ion concentration effects and improved selectivity for oxygenated products at lower overpotentials, and new fundamental insights on steering selectivity and electron transport remain to be uncovered. Nanostructuring photocatalysts can also introduce new photon scattering and electron transport phenomena that will be further explored in existing and emerging systems.



Leaf vein structure transporting nutrients over the entire leaf surface

Bio-inspired flow field transporting reactants over the entire active area

Reactant distribution over the bio-inspired flow field (numerical results)

Figure 3.22. A bioinspired approach to developing flow fields that improve mass transport in electrochemical devices. | Adapted from N. Guo et al. 2014. *Intl. J. Hyd. Energy* 39, 21185–21195, with permission from Elsevier

The discovery of new hierarchical electrocatalyst morphologies can be implemented more broadly, e.g., in porous electrode architectures, such as gas diffusion electrodes (GDEs) in which reactions occur at triple-phase boundaries; the transport of CO_2 to the catalyst is paramount. Building off knowledge in polymer electrolyte membrane technologies, research on flow fields will be necessary to improve the delivery of reactants such as CO_2 and H_2O to catalysts supported on GDEs. Research on polymer membrane and ionomers aimed at understanding ion transport in these systems will be crucial.

Modeling tools and experimental methods linking atomistic phenomena and macroscale transport

There is a great opportunity to understand atomistic phenomena and macroscale transport in such complex 3D electrode architectures by integrating modeling efforts with experiments for validation. While individual physics-based models exist (molecular dynamics, electric field models, fluid flow models, chemical kinetic reaction models), coupling is challenging because all of these models operate on different time and/or length scales. Multiscale models should be developed that are able to accurately capture the physics of systems by combining existing and emerging methods with no discontinuities. In particular, significant effort should be dedicated to the development of theoretical methods to model flow fields in three-phase systems. Initial efforts could link the catalysis occurring in the Helmholtz plane with transport modeling of ions within the boundary layer, leveraging recent successes in using molecular dynamics to describe the electrified solid-electrolyte interface and diffusion modeling. These computational efforts should be coupled to experimentally measured partial current densities to accelerate the development of these models, which should involve improved algorithms to understand flow fields in three-phase systems. Improvements in multiscale modelling will eventually be applied to understand undesired transport phenomena such as product and reactant crossover, to minimize cross-contamination and product loss. As higher experimental current densities are reached (e.g., 1 A/cm^2), heat and bubble management will also need to be described in multiscale models. In synergy with modeling efforts, a suite of existing and emerging in situ and operando tools, including x-ray techniques (diffraction, absorption, tomography, ambient pressure x-ray photoelectron spectroscopy) at both synchrotrons and emerging free-electron lasers, environmental scanning and transmission electron microscopies (liquid/electrochemical), neutron scattering and tomography, vibrational spectroscopies (infrared, Raman) should be developed to probe complex interactions with space and time resolution at both molecular and macroscopic levels under reaction conditions.

The effect of low-grade CO_2 sources on system performance needs to be probed at all scales to understand effects from contaminants such as organics, gas traces (e.g., O_2, CO, H_2S, NH_3, HCl, NOx, SOx), solid impurities, and metal impurities (e.g., mercury). Accelerated durability testing protocols need to be developed, along with associated computational modeling of degradation pathways to facilitate designs that minimize deleterious effects. Improved power supplies/technology are needed for large-scale electrolysis to circumvent inefficient DC to AC to DC power conversion with built-in safety mechanisms to protect the system in the event of power/feed surges.

Integration, cascading processes, and coupling

There is great opportunity to develop integrated one-pot approaches that combine capture, conversion, product separation, and/or reagent recycling, because such integration can potentially avoid multiple energy wells to arrive at the end product of interest. Examples of initial approaches include CO_2 (photo)reduction in a carbon capture medium, or integrating low-temperature CO_2/product separation processes into CO_2 electrolyzers for process intensification. Cascading/coupled systems should be explored using a combination of electro-photo-thermal-bio processes that first convert CO_2 into products such as CO or $HCOO^-$, which can be further reduced to methane, methanol, or C2+ products (Figure 3.23). For instance, high-energy-efficiency CO_2 → CO electrolyzers could provide a feed of either CO or syngas to a Fischer-Tropsch reactor, CO electrolyzer, or a microbial reactor, using the advantages of each catalytic system.

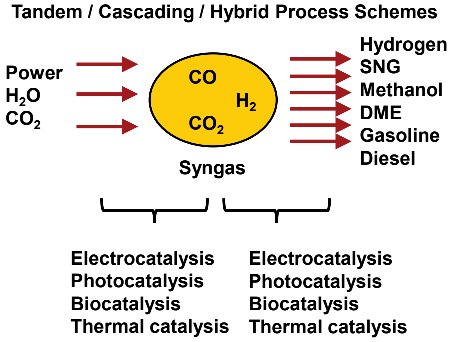


Figure 3.23. Hybrid processes that couple electro-, photo-, thermal-, and bio-catalysis provide intriguing opportunities to achieve desired product selectivity, reaction rates, and process cost-effectiveness. | Image courtesy of John Bogild Hansen (Haldor Topsøe A/S)

Technology Impacts

Understanding multiscale phenomena has broad implications for many processes involving chemical transformations, whether heterogeneous, homogeneous, electrochemical, or photochemical. Successful outcomes will include robust systems that make the best use of advanced catalysts capable of using sunlight and/or electricity for the effective conversion of CO_2. Advances in this field will have a positive impact on a range of diverse industries, from batteries to pharmaceuticals to consumer electronics.

Advances in the areas specified above will lead to CO_2 conversion configurations that are able to efficiently provide all the feeds (reagents such as CO_2 and water; electrons / photons to drive the process) and remove all the products at a sufficient rate. Improved understanding of and control over the transport of species (photons, electrons, CO_2 feed, products) over multiple scales is expected to lead to higher energy efficiency and product yields for CO_2 utilization by electrochemical and photochemical conversion. Such advances have the potential to lead to carbon-based products at a cost lower than current production methods. At the same time, converting CO_2 into C-products (renewable source) enables sustainable chemical and materials manufacturing and distributed production.

Conclusions

This PRD highlights key opportunities toward developing high-energy-efficiency CO_2 reduction systems that have the potential to greatly impact science and engineering as well as CCUS technology. Atomic-scale insights from PRD 3.5.1 will synergize with understanding of the multiscale phenomena that occur during electrochemical and photochemical CO_2 reduction. Establishing the fundamental scientific underpinnings for controlling electrode architectures, transport, and stability at the systems level will lead to high-energy-efficiency systems that can sustainably convert CO_2 to fuels and chemicals at both distributed and large production scales. Leveraging these insights on system design, there are great opportunities to hybridize processes through integration (capture, conversion, product separation, reagent recycling), cascading processes, and coupling (electro-photo-thermal-bio).

3.6.5 PRD U-5: Accelerating Carbon Mineralization by Harnessing the Complexity of Solid–Liquid Interfaces

Energy-intensive industries are at the core of the development of modern society. In rapid development of new production pathways to transform these industries into large-scale carbon sinks lies the future of carbon mineralization as a climate change mitigation solution. One pathway to achieve this objective is the development of energy-lean industrial-scale processes that can accelerate what nature does over millennia by several orders of magnitude. It is remarkable that the development of a solution that could help remedy global climate change is hampered by a current lack of understanding of the mechanisms that occur at the molecular scale. Indeed, unraveling the fundamental mechanisms that drive carbon mineralization reactions, particularly near solid–liquid–gas interfaces is the missing link to deploying carbon mineralization as a real-world mitigation solution to climate change. There is an urgent need to bridge this knowledge gap, which defines this PRD, to fast-track the development of technological solutions that can permanently mineralize large quantities of anthropogenic CO_2.

Scientific Challenges

Development of new production pathways that will transform energy-intensive industries into large-scale carbon sinks offers promising prospects for making carbon mineralization a real-world climate change mitigation solution. Imagine mining processes that produce the metals so critical to the modern way of life from host rocks while permanently binding anthropogenic CO_2 to the host rock itself. Conceive a built environment that uses high-performance materials produced using anthropogenic CO_2.

Carbon mineralization is a naturally slow phenomenon. However, it has been observed to proceed at rates orders of magnitude faster than is predicted by conventional models under specific conditions. These high reaction rates cannot yet be sustained to achieve high conversion rates, nor are they predictable. Achieving a comprehensive understanding of reactive mass transport phenomena in carbon mineralization systems is the key to harnessing the full potential of carbon mineralization as a large-scale CO_2 mitigator.

Figure 3.24 captures the complexity of solid feedstock/fluid/CO_2 reactive systems. Unlocking the complexity of these systems requires major research that will eventually lead to a mechanistic understanding and predictive modeling of elementary carbon mineralization reactions at the molecular level.

Research Directions

Figure 3.25 sets the scene for the scientific challenges associated with carbon mineralization phenomena. It shows a feedstock material, mine tailings in this case, through which CO_2-rich flue gases are injected along with a brine solution to promote the formation of solid carbonates that will permanently bind CO_2. This complex reactive system embeds a great number of coupled elementary phenomena that present multiple challenges in terms of characterization, understanding, and modeling.

The research needed to tackle these challenges and develop carbon mineralization processes is multifaceted. It includes

- Reaching a mechanistic understanding of elementary carbon mineralization reactions at the molecular level
- Developing phenomenological models that can predict the dynamic speciation of any solid feedstock/fluid/CO_2 system under a wide range of conditions, providing the basic knowledge to devise innovative carbon mineralization pathways and control reaction rates
- Collecting broad-spectrum internally consistent and validated thermodynamic and kinetic data associated with carbon mineralization of feedstocks, focusing on transfer phenomena at solid–fluid interfaces
- Developing broadly available online high-resolution investigative tools for local mass transfer measurements and phase characterization

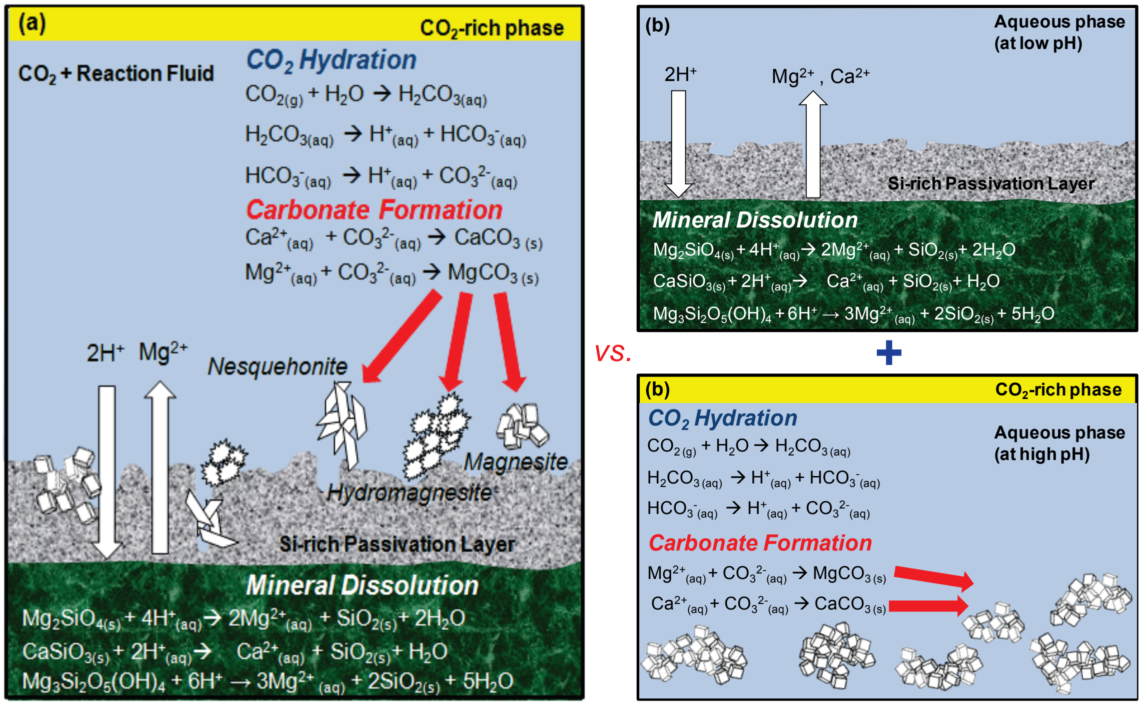


Figure 3.24. The complexity of phenomena that underlie carbon mineralization. | Reproduced from *Carbon Dioxide Utilisation: Closing the Carbon Cycle*, P. Styring, E. A. Quadrelli, and K. Armstrong, eds., G. Gadikota and A. A. Park, Accelerated carbonation of Ca- and Mg-bearing minerals and industrial wastes using CO_2, 115–137. Copyright 2014, with permission from Elsevier

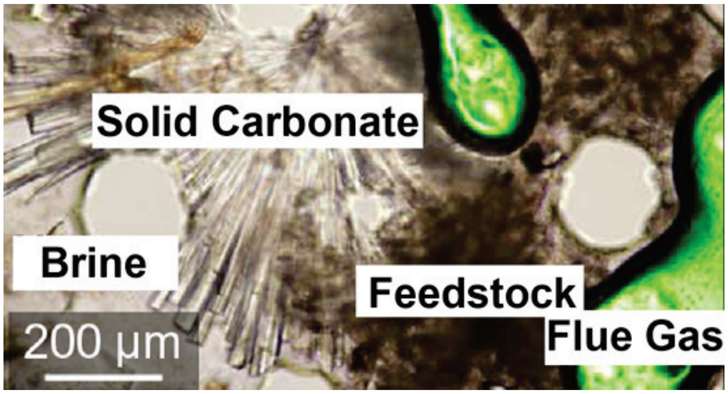


Figure 3.25. Microfluidics carbon mineralization experiment. | Reproduced from *Chem. Geol.* **463**, A. L. Harrison et al. 2017. Changes in mineral reactivity driven by pore fluid mobility in partially wetted porous media, 1–102.Copyright 2017, with permission from Elsevier

Besides the scientific dimension of this carbon mineralization PRD, the collection, management, and dissemination of this new knowledge are essential. Capitalizing on a data collection effort requires setting an open-access library of thermodynamic and kinetic data for carbon mineralization feedstocks and products, deriving standard formats for online submission of data sets that are readily implementable in thermo/kinetic databases, creating a international data review panel, and possibly devising a motivating credit system for submitting authors.

Technology Impacts

The fundamental nature of this PRD, which addresses both fundamental understanding and observation of carbon mineralization is expected to have numerous high-level scientific impacts. As the relevance of the underlying scientific challenges is not limited to the carbon mineralization field, research developments will also provide bases for advancing other communities confronted with complex mineral/liquid/gas systems. One such environment would be geothermal energy production, which is confronted with complex issues associated to silicon-rich mineral phases.

The main scientific impacts expected include (1) providing internally consistent and validated thermodynamic, transport and kinetic data for carbon mineralization systems; (2) inventing novel high-resolution real-time instruments for characterizing dynamic solid–fluid systems; and (3) improving the understanding of solid-liquid-CO_2 reaction pathways under a broad range of conditions.

Not losing sight of the bigger picture—i.e., the rapid deployment of carbon mineralization to offset climate change through mitigation of CO_2 emissions—the fundamental research promoted by this PRD is expected to have direct impacts on CCUS technology. These high-level impacts include (1) fast-tracked novel, market-ready net positive energy carbon mineralization processes, (2) a ranked list of high-potential carbon mineralization feedstocks, and (3) input-output data for economic and environmental life cycle assessment of carbon mineralization processes.

Conclusions

Energy-lean industrial-scale carbon mineralization processes that permanently bind CO_2 emissions into stable solid materials are an important asset in the portfolio of CCUS solutions. It is remarkable that the pathway to developing such large-scale processes lies in the ability to understand and predict carbon mineralization reactions at the lowest scale. Reaching a high-level of understanding of carbon mineralization reactions is a challenging and stimulating endeavor. It is, however, within the realm of scientific inquiry; and there is no doubt that international collaboration across a large spectrum of scientific communities would lead to the deployment of successful carbon mineralization processes on the time scale required to make an impact on greenhouse gas mitigation efforts.

3.6.6 PRD U-6: Tailoring Material Properties to Enable Carbon Utilization and Storage in Products

Carbon mineralization converts CO_2 into carbonate reaction products, thereby permanently storing it in a thermodynamically stable form. Coupling carbonate formation with the manufacturing of useful products allows CO_2 utilization to be linked to a process that generates economic value and reduces raw material use and associated CO_2 emissions. Many naturally occurring and industrially manipulated materials can be treated with CO_2 and take forms that satisfy applications in the built environment. To put mineralization into practice, innovative and fundamental research is required to overcome several technology challenges. Better understanding of process parameters and material composition, and their relationship with product properties and performance, will aid in meeting stringent performance requirements and allow the prediction of the long-term performance of the building products. This knowledge will come from the use of novel material characterization techniques both online and offline. Better performance will come from pre- and post-treatments that not only improve product properties but also allow the extraction and utilization of deleterious and/or valuable by-products.

Scientific Challenges

Carbon dioxide can be used to create valuable and useful products across a wide variety of applications and impacts. Potential products can include structural materials (e.g., concrete and mortars), nonstructural materials (e.g., for road-base, erosion, sea, and flood protection barriers), and protective coatings (e.g., paints and polymers). The overall mitigation potential of currently identified applications for the built environment exceed 2 Gt of CO_2/year. Meeting this potential requires predictable and controllable processes that can consistently produce products that satisfy appropriate performance criteria.

We presently have a general understanding that carbonates can play a role in (1) providing cementitious binding of the components of the building product, (2) providing structural support for building products (as aggregate or filler), (3) stabilizing the leaching of mobile heavy metals, and (4) stabilizing the alteration of meta-stable mineral phases. However, we lack mechanistic understanding, especially at the nanoscale and microscale levels, of the influence of carbonation conditions (e.g., temperature, pressure, presence of minor and trace chemical species) on significant variations in product quality and observed performance. Linking product performance to micro-structure, geochemistry, and mineralogy is the key to achieving consistency.

An additional challenge is the incorporation of carbonated waste materials, and carbonation by-products, in building products. Barriers to utilization include leaching of toxic elements or the presence of deleterious meta-stable minerals. Advances in research toward these materials can significantly expand the market applicability of CO_2-treated alkaline waste materials to serve as conventional building materials, or even as high-value and specialty products.

Research Directions

The research will be directed toward understanding the following topics: (1) real-time monitoring of product properties during synthesis, (2) nano-characterization of feedstocks and products, (3) structure-property-performance relationships, (4) pre- and post-processing treatments, and (5) long-term performance and durability prediction.

Development of new monitoring and analysis techniques for characterizing the properties and performance of carbon mineralization systems is needed to obtain fundamental and reliable understanding of structure-property-performance relationships. These must include real-time monitoring of carbon mineralization product properties during reaction, as inefficiencies in the materials synthesis processes and limitations of product quality are primarily hindered by transient, interfacial, and nanoscale phenomena. Real-time methods are thus crucial to allowing the control of reaction pathways and tailoring product properties.

Research paths include determining how controllable manufacturing factors (e.g., temperature, pressure, system chemistry) and product output characteristics (e.g., mineralogy, shape, particle size) can impact short- and long-term product performance. Examples of real-time monitoring include tracking of volume changes in porosity and pore size; the evolution of gas and liquid permeability; and the formation of stable and meta-stable, crystalline, and amorphous phases and chemical species. Techniques for real-time monitoring include the use of x-rays, photons, electrons, and neutrons for determining bonding energies and lengths, elemental distribution, molecular orientation and organization, and spatial mapping.

These and related techniques (e.g., nano-indentation; see Figure 3.26) can also be used for ex situ nano-characterization to examine feedstock properties and product properties following processing, accelerated weathering, and long-term use in the built environment. The goal is to achieve breakthroughs in the modeling, prediction, and design of product properties and performance, particularly linking the microscale to the macroscale. For instance, extending carbonation process-based interface transition layer theory can enable directional control of carbonated products.

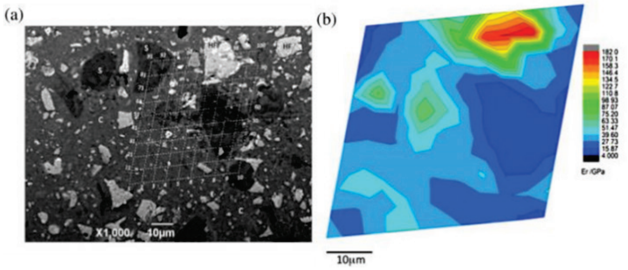


Figure 3.26. Nano-indentation grid testing to assess localized mechanical properties. | Reproduced from *Cement Concrete Res.* **88**, L. Mo et al. 2016. Mechanical performance and microstructure of the calcium carbonate binders produced by carbonating steel slag paste under CO_2 curing, 217–226. Copyright 2016, with permission from Elsevier

Reaction pathways and tailored product properties can also be controlled by adopting pre- and post-processing treatments that condition the feedstock for the carbon mineralization process, that separate problematic or valuable components before or after the reaction, and that improve the quality of the product for the intended application. It is important also to examine the impacts of feedstock properties and feedstock replacement on product performance, and to assess the potential for innovative symbiotic combinations of feedstocks. Potential treatments to achieve these objectives can include mechanical and ultrasonic activation, alkaline additives, heat and microwave treatment, chemical or biological lixiviant processes, admixtures, and solid–solid separations.

Turning waste materials and low-value complex minerals into building products also presents unique opportunities that should be pursued. These include

- process integration during cooling of thermal alkaline waste and during comminution of bulk minerals
- the removal of various CO_2-containing flue gas pollutants (e.g., SOx/NOx/PM) as captured minerals
- the recovery of valuable materials from carbon mineralization by-products or co-products (e.g., Ni, Cr, Ti, V, rare earth elements, metallic oxides and salts, reactive amorphous silica);
- the encapsulation and mineral trapping of toxic compounds
- the incorporation of biofibers and bio-residues into CO_2 neutralized building materials that prevent the degradation of organic materials

Technology Impacts

The ultimate impact of such research will the development of reliable, cost-effective processes for generating construction materials that meet performance criteria while permanently storing CO_2 on a gigatonne scale. In addition, there is great potential for extracting and recovering valuable by-products that can be of use to various other industries and applied to various other nonbuilding products. By tailoring products, co-products and by-products, new application avenues can also be identified and exploited. Insights of this research will also be applicable to the use of carbonation for environmental remediation and for subsurface mineral trapping.

Obtaining a better understanding of how process conditions affect product properties is critically important for meeting performance requirements such as strength, durability, and leaching stability and for informing studies on economic feasibility and life-cycle analysis. When fundamentals of synthesis processes are poorly understood, process technologies are inadequately designed, resulting in weak economic and environmental impact assessments. Building materials are valuable products but are generated by industries with tight margins and strong competition. Therefore, efficient process design and confidence in product performance is critical for making technologies competitive and achieving their CO_2-sequestration capacity potential. Likewise, potential novel products and by-products that can be obtained via carbon mineralization (e.g., precipitated calcium- and magnesium-carbonates, and nano-silica) can be better tailored and can find more valuable applications if their production is understood at the fundamental level and controlled at the microscale level whereas their performance is prognosed for the long term.

Carbonated materials that provide suitable structural/mechanical performance can lead to reduced use of carbon-intensive materials traditionally used in the production of cement- and concrete-based building materials, coatings, polymers, rubbers, papers, and other mineral-containing products. Carbon dioxide can also enhance and accelerate the hydration of conventional Portland cement, lead to replacement of cement by a CO_2-activated binder for precast and cast-in-place applications, and rapidly cure 3D-printed building structures. Finally, waste and CO_2 co-utilization also leads to the reclamation of land presently used for waste storage, remediation of soil and groundwater, and recovery of valuable materials trapped within low-value waste materials.

Conclusions

Carbon dioxide utilization in the built environment provides impactful, permanent, and economically driven CO_2 storage. Studying solid–liquid–gas interfacial interactions and the real-time effects of process parameters and feedstock properties will unlock the barriers to storing globally significant amounts of CO_2, in addition to providing useful, cost-effective, and carbon-neutral or -negative materials for everyday life that replace carbon-intensive traditional materials.

3.6.7 PRD U-7: Tailoring Microbial and Bioinspired Approaches to CO_2 Conversion

Microorganisms can convert $CO_2$with the power of the sun or via chemical reducing power from other resources into fuels and value-added products. The conversion of single carbon building blocks into more complex molecules by biological systems is collectively referred to as C1 metabolism. Leveraging the recent technological revolution in systems and synthetic biology, the complexity of living systems can now be harnessed to address our most pressing global challenges, in industrially scalable and economically sustainable ways. Researchers are starting to accurately understand, model, and engineer living systems as networks of genes, enzymes, products, and even ecological interactions. This will lead to intensified, robust bioprocesses, with high rates and efficiencies, and a broad portfolio of products. These efforts will enable CO_2 to become a valuable feedstock for bioconversion processes.

Scientific Challenges

Microorganisms have evolved catalysts for a multitude of chemical reactions. They perform complex transformations at ambient pressures and temperatures. Collectively, each year they turn over more CO_2, through photosynthesis, than humans emit from fossil fuel burning. Examples of products of microbial C1 metabolism include nutritionally valuable proteins, lipids, and carbohydrates as well as fuels and commodity and specialty chemicals. Although C1 metabolism appears to proceed via simple reactions, their simplicity is deceptive. Each microbial cell makes use of a complex cascade of reactions. Moreover, microbes in nature rarely work in isolation but interact with a multitude of other organisms. Grasping the complexity of microbial cells and ecosystems (often referred to as “microbiomes”) is daunting, to say the least.

In view of this evolved complexity, it is not surprising that it has proved to be challenging to engineer robust, high-rate microbial processes for CO_2 conversion. Despite much progress, the details of microbial metabolism often remain a black box; and only a fraction of the natural microbial biodiversity has been unlocked. Yet, there is evidence that biosystems possess immense potential for contributing to CO_2 utilization at rates and scales of global consequence. Accessing biodiversity—in conjunction with deepening the understanding of C1 metabolism and tapping into the basis of robustness of natural microbial ecosystems—will be needed to realize productive commercial microbial systems that convert CO_2 into valuable feed, fuel, and chemical products.

Intensification of bioprocesses is essential to reduce costs and often depends on enhancement of gas/liquid transport rates and rates of photon capture for light-dependent conversions. Separation of products and microbial biomass from process water also significantly contributes to costs and energy requirements. In nature, these challenges are overcome through the use of specialized enzymatic catalysts (e.g., enhanced CO_2 hydration by carbonic anhydrase), adaptation to environments favoring the desired process (e.g., high pH, temperature) or associations with partner organisms. Such strategies offer inspiration for new directions for process design, including hybrid approaches involving chemical-/electro-/photocatalysis and smart materials.

Research Directions

1. System-level understanding of physiology, metabolism, energetics, and ecology of key microbes and consortia

To maximize conversion rates and efficiency and grow the product portfolio, research is required to improve understanding of C1 metabolism with energy from sunlight or reducing agents, and conversion into desired products. Deeper understanding will allow better quantification of the rates and efficiencies of the metabolic pathways. This will guide targeted microbial engineering to improve energy conservation, cofactor and redox balancing, and metabolic regulation—which in turn will allow advanced process designs that maximize energy and carbon yields in desired products. For phototrophs, this means the identification (via bioprospecting) or generation (via directed evolution, mutagenesis, or genetic modifications) of organisms or consortia with high areal biomass productivity in outdoor cultivation systems.

The recent revolution in "omics" technology must be applied to drive big-data acquisition and modeling of C1 bioconversion systems at the level of genes, enzymes, metabolites, and ecological interactions. This will dramatically accelerate the pace of discovery and heighten understanding of the determining factors for process rates and of the robustness of such bioconversion systems. Omics will also enable much more effective mining of the vast realm of uncharted microbial diversity and microbial community engineering. The resulting new strains could target waste streams from different industries or processes, each with its specific physical/chemical challenges.

2. Fundamental improvement of biological one-carbon metabolism

Genetic and metabolic tools need to be developed and optimized for existing and new model organisms capable of converting C1 molecules to biomass and products at low cost. Combining industrially robust microorganisms with C1 assimilation routes that operate in other organisms is a promising way to expand the metabolic versatility of converting CO_2 into valuable chemicals. Furthermore, the discovery of new enzymes and metabolic pathways for assimilating C1 compounds could lead to unparalleled efficiency. This requires fundamental understanding of enzyme mechanisms and integrative modeling efforts to uncover the thermodynamic and kinetic limitations and potentials of synthetic metabolic structures. These new enzymes and pathways could be established in already existing C1 assimilating microbes or could be used to transform selected organisms into efficient biofactories.

3. Bioinspired approaches to improve mass transport and product separations while minimizing water use

There exist microbial ecosystems that convert gases such as CO_2 and CO, or important energy carriers such as H_2, at extremely high rates, providing inspiration for how we might improve industrial bioconversion. Photosynthetic microbial communities in upwelling zones, coral reefs, and alkaline soda lakes are three examples powered by the sun. Ocean hydrothermal vents, also extremely productive ecosystems, make use of reducing power from the Earth's interior. What these ecosystems have in common is that they realize high carbon fixation rates by improving mass transfer. Transfer of essential nutrients (nitrogen, phosphorus) is enhanced in upwelling zones, supply of reducing minerals is enhanced near hydrothermal vents, and CO_2 supply is enhanced in soda lakes characterized by high pH and alkalinity. The commonalities among these ecosystems will provide inspiration for the next generation of bioindustrial processes. Advanced gas-exchange systems and bio-emulating synthetic materials would overcome existing limitations. For example, the application of carbonic anhydrase could accelerate CO_2 dissolution and microbial productivity. If mass transfer can be improved sufficiently, we can realize the use of dilute CO_2 directly from air.

Dewatering, biomass separation, and minimizing the use of freshwater requires further improvement. The application of microbes in brackish water or seawater, and in water from other nonpotable sources available worldwide, would help reduce pressures on freshwater supplies. Understanding microbial interactions will help improve bioseparation processes. For example, cyanobacterial mats, or the induction of autoflocculation, could be used to improve biomass separations from water.

4. Hybrid catalytic/biological systems.

Both photons (sunlight) and chemical energy carriers (e.g., hydrogen, carbon monoxide) can provide power to microbes for CO_2 fixation and conversion. Thus, hybrid approaches can be envisioned whereby photons or renewable electricity are converted catalytically or biologically to hydrogen or another energy carrier, followed by a second microbial or catalytic step converting the energy carrier and CO_2 into value-added products. Alternatively, value might be added to microbial products or biomass by chemical or thermal approaches.

Research focused on the interaction between electro- or thermo-catalytic systems and biological processes is needed. Direct electron transfer from electrodes to microbial cells might also be considered, as well as electrochemical production of molecules that dissolve well in water, such as formate and methanol.

Technology Impacts

These research directions will lead to intensified, robust bioprocesses, with high rates and efficiencies, and a broad portfolio of products. In turn, intensification will reduce costs, leading to conversions with high technoeconomic feasibility and commercial potential. Feed, fuels, and base chemicals will be examples of viable bioproducts. Initially, this new generation of bioprocesses will be applied mainly to industrial waste streams, for example, flue or stack gases from steel manufacturing or power plants. Direct air-capture of CO_2 will become the next target, with the ultimate aim of combining bioprocesses with carbon sequestration to realize "negative emissions."

Conclusions

- Microbial processes have enormous potential for CO_2 conversion.
- Successful engineering of robust and efficient bioprocesses is challenging because of their biological complexity and a lack of fundamental understanding of underlying metabolic processes.
- Rapid technological developments in omics technology and synthetic biology enable us to effectively find or create new organisms or consortia to realize higher volumetric conversion rates and/or higher areal biomass productivities.
- Rates of bioprocesses are often limited by transport processes. Transport processes can be improved using bioinspired approaches.
- Hybrid chemical and microbiological approaches may combine the best of both worlds.

3.6.8 PRD U-8: Hybridizing Electrochemical and Biological Processes for CO_2 Conversion to Fuels, Chemicals, and Nutrients

The objective of this PRD is to develop the fundamental science that will allow the combination of electrochemical and biological processes to produce fuels, chemicals, and nutrients economically from inexpensive feedstocks: waste CO_2, water, and renewable energy. Electricity is the main energy currency, to which multiple renewable sources are converged. This situation is expected to remain in the future, regardless of any new energy source that might be developed. Electrochemical processes are highly efficient in generating hydrogen from water or reducing CO_2 into the C1 energy carriers CO and formate ($HCOOH/HCOO^-$) [Martin et al. 2015; Pletcher 2015]. However, electrochemistry, by itself, is not good in converting these energy carriers into the complex molecules used in everyday life. Biology is efficient in using these energy mediators in valuable fuels, chemicals, and nutrients. With the falling price of sustainable electrical energy, a hybrid approach that combines these electrochemical and biological processes provides a rare opportunity to address a multiplex of global macro-challenges through the production of high volumes of a broad variety of useful commodities at minimal cost using CO_2 as the sole carbon feedstock. Nevertheless, the integration of electrochemical and biological processes presents numerous challenges that have yet to be fully addressed. To realize the full potential of the hybrid system, fundamental research is required to understand, manipulate, and perfect the interaction among the system's units. Fundamental research is further needed to optimize the activity of each segment of the hybrid system: (1) gain insight into the physiology and biochemistry of H_2, CO, formate-consuming, and other chemolithautotrophic organisms, followed by synthetic metabolism approaches to perfect their utilization; (2) research the durability, robustness, and energetic efficiency of electrochemical systems that generate the energetic mediators while reducing the use of rare earth metals.

Scientific Challenges

The integration of electrochemical and biological operations is neither common practice nor trivial. The efficiency and longevity of each operation is dynamically influenced by the other process and its by-products. The precise nature and magnitude of these incompatibilities must be defined, modeled, and addressed through process modification and additional ameliorating operational steps. In each process operation (electrochemical and biological), maximizing the selectivity of the conversion of feedstock to product is critical. Also, overcoming the deleterious influence of undesirable side products from each operation on the other process, and ultimately on final process yields and stability, is essential [Li et al. 2012]. The integrated electro-bioprocess should also be studied and optimized in terms of gas-to-liquid transfer of the gaseous mediators (H_2, CO) and control of the rate and concentration of the soluble mediator (e.g., formate, metals). The microbial physiology and biochemistry of the microbes should be deciphered and engineered to fit the electrochemical parts, which include resilience toward electrochemical by-products and optimal consumption of fluctuating concentrations of the energetic mediators. Electrochemical systems should be studied and engineered to be tolerant toward the products of the microbial metabolism and avoid degrading them at the cathode or anode.

Research Directions

A multidisciplinary research effort is required to address the challenges manifested in integrating electrocatalytic and biological processes (see the sidebar "The Need for Multidisciplinary Research"). It requires specialists in fields such as electrochemistry, chemical engineering, bioprocess design, microbiology, metabolic engineering, and computational/mathematical modeling. We particularly envision the following research directions:

- **Mechanistic studies.** Separate research activities have already advanced both the area of electrocatalytic process development and the biological conversion of C1 feedstocks. However, combined studies are now required to define the physical, chemical, energetic, and engineering challenges that are manifest when these two operations are combined into a single, integrated continuous production platform. Special attention should be given to unexplored routes by which one process influences the other, either by generation of reactive by-products, or by changing the overall conditions within the integrated system.

- **Extensive modeling.** Sophisticated models that capture the biological, electrochemical, and integrated processes must be developed to identify parameters that present the greatest barriers to favorable functionality, stability, and economics. Such a modeling effort will pinpoint bottlenecks in the activity of the hybrid system and thus help to prioritize research agendas for each field of research (e.g., electrochemistry, microbiology, process engineering).
- **Eliminating poisoning and fouling.** Electrochemical and biological systems each produce various by-products that can influence, disturb, and inhibit the other. For example, reactive oxygen species produced at an anode can strongly inhibit cell growth [Li et al. 2012]. Similarly, bioproduced chemicals can poison electrode activity and reduce overall efficiency. This problem is especially challenging when extensive recycling of water and gas streams are pursued to minimize the water and energy footprint. For example, CO_2-rich by-product gases from the biological conversion of C1 gas to products may be recycled to the electrocatalyst for upgrading; yet contaminants from the biochemical reactions will be entrained in these gases. It is therefore vital to develop robust bio- and electrocatalysts that can withstand the presence of such by-products, and further engineer them for highly specific conversion of feedstock to product. In addition, it would be advantageous to explore support processes that eliminate these deleterious by-products or recycle them back into the main production line.
- **Synthetic metabolism.** Tools allowing the engineering of C1 utilizing microbes are in many cases at a nascent stage compared with those available in model sugar-fermenting organisms such as *E. coli* and yeast. Hence, developing robust and efficient genetic and metabolic tools for the engineering of C1-using microbes is of prime significance, especially in terms of sustaining feedstock to product specificity. Synthetic biology tools should be developed to enable expanding the microbial product portfolio cultivated on the energized mediators. Especially promising is the engineering of novel enzymes and pathways that could support carbon fixation and/or assimilation of CO and formate using new and efficient routes that could increase yield and productivity [Erb et al. 2017]. A metabolic engineering approach could further minimize the production of deleterious by-products and increase the tolerance of the microbial biofactories to electrochemical by-products. As the concentration of energized mediators is expected to fluctuate, it will be helpful to explore and optimize microbial metabolism at different concentrations of the feedstock.
- **Exploring natural diversity.** The current repertoire of known microbes that can grow on H_2, CO, formate, or other inorganic mediators is quite extensive and can be used to identify optimal hosts for the hybrid process. However, it is expected that the natural diversity of metabolic solutions for assimilating these energized mediators has yet to be full revealed and might hold great promise in terms of efficiency and compatibility with the electrochemical process. Hence, it is imperative to keep searching for novel microbes and metabolic capabilities that will enable improved performance. Of special interest is the discovery of microorganisms capable of withstanding the harsh conditions that might be associated with the electrochemical process (e.g., reactive oxygen species).
- **Bioprocess research of the integrated system.** The hybrid system involves three phases (gas, liquid, and solid), which complicates process integration and requires fundamental research into the in situ transfer of compounds. Special focus should be given to studying and optimizing H_2 and CO transfer to the microbial culture from the electrodes, reducing other inorganic mediators at the electrodes, and converting gaseous CO_2 into soluble formic acid. Different temperatures and pressures should be investigated and unique electro-bioreactor designs should be developed. Temporal and spatial coupling or decoupling of the electrochemical and biological processes should be investigated to identify the best approach to enable efficient processes with minimal cross interference.

The Need for Multidisciplinary Research

To enable the use of renewably produced electricity and CO_2 to produce everyday chemicals, a combination of chemical and biological expertise is needed. Chemists can now use electricity to efficiently produce small energized intermediates that can then be consumed by specialized microbes and converted into fuels, chemicals, and nutrients. This process can revolutionize production and completely decuple it from the use of fossil carbon or agricultural products.

Yet, to fully realize the potential of this production chain, interdisciplinary fundamental research is required that will involve chemists, biologists, and process engineers. Both the chemical and biological processes need to be optimized in terms of production specificity, energetic conservation, durability, and robustness. Research into novel materials could enhance the electrochemical process, and a synthetic metabolism approach could offer novel and improved microbial biocatalysts.

Of special importance is the study of interactions between electrochemical and biological processes to maximize the beneficial transfer of materials between the two and minimize deleterious inhibitory effects one process might impose on the other. This research effort should be coordinated to enable co-optimization of the two processes and thus a revolutionary system for converting CO_2 to valuable products.

Technology Impacts

The hybrid model offers several advantages compared with other methods of converting CO_2 and renewable energy to chemicals of interest:

- The technology leverages recent advances in molecular biology and microbial metabolism to create a viable route to convert energized simple intermediates–efficiently generated from electrical energy—into high-value fuels, chemicals, and nutrients.
- The technology expands the range of products that can be made from CO_2 and electricity to include complex molecules such as nutrients, flavors and fragrances, enzymes, biodegradable polymers, and pharmaceuticals.
- Capital and operational costs will be substantially lower compared with building a chemical plant to convert C1 energy carriers to high-value fuels and chemicals.
- The sustainability of bioproduction of fuels, chemicals, and nutrients is much higher via the hybrid process than using sugars or other agricultural products as feedstocks. Instead of competing with food production for the use of agricultural output, the hybrid process can be used to increase food security by producing nutrients from CO_2, water, and renewable electricity.

Conclusions

The hybridization of electrochemical and biological processes for the conversion of CO_2 and electricity into fuels, chemicals, and nutrients would provide sustainable production systems at a scale that is unachievable with current processes and feedstocks. However, numerous fundamental scientific challenges and questions must be addressed before this promise can be realized. There is particularly a need to research and optimize the integration of electrochemical and biological processes and to explore novel metabolic capabilities enabling the efficient conversion of CO_2, CO, and formate into products. It is clear that developments in multiple scientific fields are needed to deliver a productive integrated technology. With the emergence of grid-scale, low-cost sustainable power generation, there has never been a more opportune time to investigate such a hybrid process that promises a new industrial vision.

3.6.9 PRD U-9: Engineering Complex Interfaces for Enhancing Hydrocarbon Recovery with Potential Carbon Storage

The sustainable development of subsurface energy technologies is essential, as more than 82% of energy resources are derived from such environments. Significant benefits to energy and environmental sustainability can be achieved by

- using anthropogenic CO2 instead of natural CO2 for EOR from conventional formations
- replacing water with CO2 for hydrocarbon recovery from tight reservoirs (e.g., shale)
- using CO2 as a working fluid for geothermal energy recovery
- engineering fractured or nanoporous media for permanent carbon storage to increase the global volumetric capacity

To advance these areas of interest, a fundamental scientific understanding of CO_2–rock interactions at multiple scales is essential.

Scientific Challenges

Transformative advancements in the utilization of CO_2 for
enhanced hydrocarbon recovery with the potential for storage can be achieved by developing a fundamental understanding of

- complex fluid interactions in low-permeability reservoirs with chemical and morphological heterogeneity
- pressure limits on CO_2 storage
- chemophysical behaviors of fluids in confined environments at elevated temperatures and pressures
- the fate of the injected fluid

Research Directions

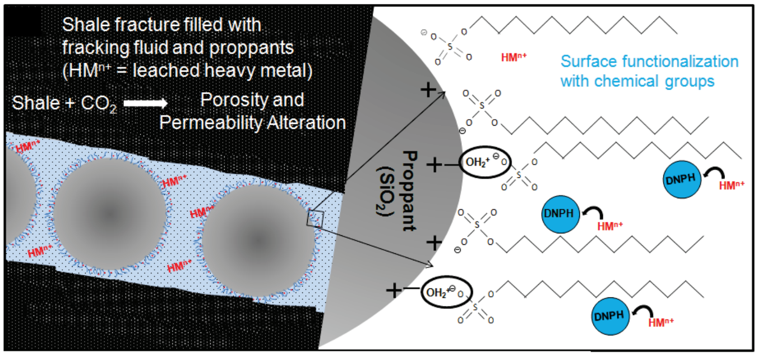


Figure 3.27. CO_2-shale-water interactions: Inducing chemical and morphological changes in shale using CO_2 for efficient gas extraction coupled with the in situ immobilization of heavy metals using chemically functionalized proppants. CO_2 will be subsequently stored in the depleted pore spaces. | Image courtesy of Ah-Hyung Park, Columbia University, and Greeshma Gadikota, University of Wisconsin

Several transformative research pathways need to be adopted for the field-scale implementation of hydrocarbon recovery from unconventional and conventional reservoirs using CO_2. A molecular-to-field scale understanding of the chemophysical behaviors of CO_2 interactions with rocks of heterogeneous morphology and chemical composition is essential for the large-scale deployment of CO_2 use for enhanced hydrocarbon recovery (Figure 3.27). Toward this end, there is a need for field-scale laboratories to evaluate the effectiveness of CO_2 as a working fluid for hydrocarbon recovery with the potential for storage. There is an emerging need for consistent protocols for laboratory- and field-scale tests to accelerate the advancement of this research area. The application of advanced multiscale in-operando synchrotron and neutron scattering, tomography, and absorption techniques are essential for developing a fundamental understanding of CO_2 interactions at complex interfaces. This understanding will be bridged by advanced computational tools at the molecular scale, laboratory-scale studies, and field-scale modeling and experimental investigations.

Another approach to enhancing hydrocarbon recovery from unconventional formations requires advanced materials discovery. The physical and chemical processes governing the interactions of the engineered materials at fluid–solid interfaces and in extreme environments need to be tuned for the optimal recovery of hydrocarbons with potential storage. Examples of advanced materials include functionalized materials, functionalized fluids, and foams (see the sidebar "CO_2 Foams for Enhanced Hydrocarbon Recovery and Fracturing").

Further, there is an emerging need to apply advanced data science approaches to achieve convergence in upscaling and downscaling studies. The use of advanced computational models and synchrotron tools for innovative field-scale techniques generates extensive data sets. Novel approaches are critical to model data across scales to develop insights that range from fundamental interfacial mechanisms to field-scale implementation.

Technology Impacts

The development of consistent experimental protocols, application of advanced data science tools, and advanced understanding of engineered and natural materials in extreme environments will be valuable in related fields such as **geothermal energy and conventional carbon storage**. The scientific understanding developed by pursuing the research directions outlined in this report has synergies with the development of novel materials for managing well-bore integrity and salt-induced precipitation for CO_2 storage, and advanced data science methodologies for conventional geologic storage and enhanced hydrocarbon recovery. Scalable development of enhanced hydrocarbon recovery using CO_2 will require the advancement of other crosscutting approaches, such as the development of CO_2 transport networks to connect CO_2 capture sites with utilization and storage sites, and development of technoeconomic assessments of the CO_2 offset achieved.

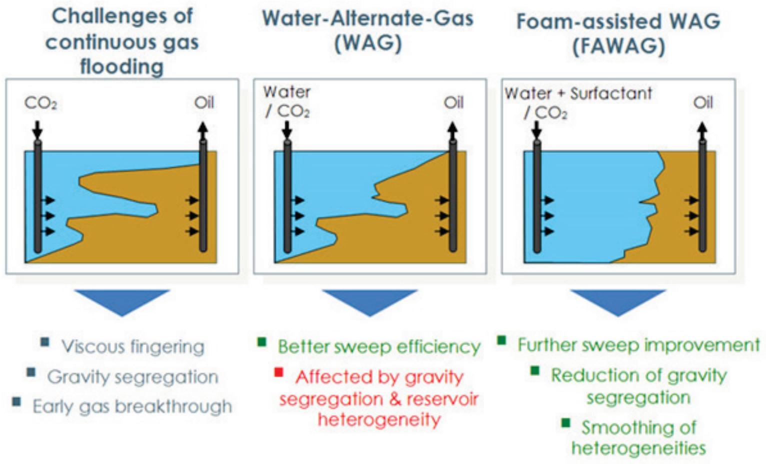
Conclusions

The extensive use of CO_2 for sustainable subsurface energy recovery with potential storage will result in reduced use of water for energy generation and create a market for anthropogenic CO_2 as a working fluid for energy recovery. From a scientific standpoint, it will lead to the development of advanced materials discovery, application of in-operando characterization techniques to mimic subsurface environments, and a fundamental understanding of the chemophysical behaviors of CO_2 in confined nanoporous environments.

CO_2 Foams for Enhanced Hydrocarbon Recovery and Fracturing

For high oil extraction efficiency, CO_2 is generally employed; it is supercritical at reservoir conditions and helps recovery through swelling and viscosity reduction (Lake 1989; Orr and Taber, 1984). However, the efficiency of the overall process is reduced by the buoyancy of CO_2 because of its lower density compared with the host brine in the aquifer, viscous fingering, and CO_2 channeling through high-permeability layers. To overcome these problems, CO_2 is injected as a foam, which reduces the gas mobility in high-permeability zones such as fractures and gravity-override regions that contain little oil. Moreover, the foam is designed to break in the presence of residual oil, enabling contact between the oil and the gas to allow oil capture (Rossen 1996). Foam is identified as a complex fluid in which the gas phase is segregated in bubbles separated by thin films (called lamellae) stabilized by surfactants.

Foam with a gas fraction (fg) of 0.5–0.6 has been successfully applied; but larger fgs, up to 0.8–0.9, can be reached by using nanoparticles instead of or in conjunction with traditional surfactants (Prigiobbe et al. 2016). One of the new applications of CO_2 foam as a fluid is in hydraulic fracturing for shale-gas production. Here, the major advantages are the smaller volume of water required to perform the operation and the rheological properties of the foam that allow a better control of fluid mobility in fractures. Employing smart nanoparticles to stabilize the foam could significantly reduce the consumption of water, particularly in arid regions, and maximize the use of CO_2 .



Schemes for injecting CO_2 foam for EOR applications and its advantages compared with continuous CO_2 flooding. | Image courtesy of EOR alliance

The major challenges of this approach are

- Understanding the behavior of a CO_2 foam moving through media of variable permeability (nanoporous and microporous and fractured) at the reservoir conditions of temperature, pressure, and salinity
- Understanding the reactivity between CO_2 foam and the shale to predict carbon storage

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4. Carbon Storage

Subsurface storage currently represents the only viable approach to isolating large volumes of CO_2 from the atmosphere. There has been continuing improvement in the knowledge base needed for successful storage, especially from several megaton-scale demonstration projects over the past two decades. In addition, we have learned significantly from CO_2-enhanced oil recovery how CO_2 behaves in different geologic formations, and what types of chemical and physical interactions can occur between CO_2, water, hydrocarbon, and minerals. A key issue for the future is how to improve confidence that it is possible to take subsurface storage to the gigaton/year level needed to substantially reduce emissions. This theme assesses the most pressing research needs for CO_2 storage, especially in the context of the need to ramp up to large scale. The panels identify research advances that are required in four specific areas, including (1) injectivity and capacity; (2) monitoring, verification, and performance metrics; (3) forecasting and managing induced seismicity; and (4) well integrity. The proposed research areas are described in panel reports and nine Priority Research Directions (PRDs).

Panel S1: Injectivity and Capacity

Accurate estimation of injectivity and storage complex capacity is needed to match CO_2 sources to storage sites, determine the number and type of wells, and improve confidence that the reservoirs can accept CO_2 in the amounts and at the rates necessary over an expected project lifetime. Injectivity at the site scale is ultimately needed to ensure storage capacity, but estimation at basin and larger scales is also needed to evaluate storage resources. Injectivity can depend on many factors and may evolve over the course of injection as the free-phase plume grows and the pressure front expands to encounter reservoir baffles and hydrologic (reservoir compartment) boundaries, potentially over many years of injection. Storage capacity is also influenced by the geophysical and hydrologic characteristics of the site. Geological aspects include reservoir and seal architecture and lithologic/hydrologic properties of the storage complex. Hydrological aspects include two-phase (or sometimes multiphase) residual trapping and capillary exclusion under injection and buoyant migration conditions. The geomechanical properties of the reservoir and seal(s) limit capacity through the need to maintain low risk of induced seismicity or fracturing that could affect cap rock integrity. Geochemical dissolution and mineralization rates can become a more prominent factor in the storage capacity of more reactive rock types such as basalt and volcanogenic sandstones.

Panel S2: Monitoring, Verification and Performance Metrics

Effective subsurface storage of CO_2 entails monitoring and accounting for injected CO_2. Monitoring is required to reasonably demonstrate that the injected CO_2 is contained securely within the geologic storage site, and should be integrated with a risk management plan that includes mitigation protocols for preventing or minimizing impacts on the environment or resources. Advances in monitoring are needed to enable storage performance verification at a higher level of certainty, both during and following injection operations. Areas where basic research could lead to critical improvements include sensor and tracer technology, remote monitoring, joint inversion methods for geophysical data, and optimized design of monitoring and information systems.

Panel S3: Forecasting and Managing Induced Seismicity

A growing body of evidence from fluid disposal operations suggests that induced seismicity is a risk that should be assessed, monitored, and managed as needed at every injection site. Understanding the initial stress field and the impacts of formation geomechanical properties and mechanisms that cause events might be used for forecasting hazards. Advances in understanding of fluid and pressure-induced microseismicity could aid in developing hazard forecasting tools and protocols that could be used by operators to manage the risk of induced seismicity and associated impacts to the environment and resources.

Panel S4: Well Integrity

Well integrity is a primary concern for storage integrity because wellbores can act as conduits for fluid migration from the storage reservoir to protected resources or the surface. Well leakage can occur in active or inactive wells, new or old. Old abandoned wells are of particular concern because they likely were plugged using procedures and materials that are antiquated by today's standard. Current technologies for assessing well integrity issues such as cement bonding, voids, and casing integrity are limited because of cost, measurement limitations, and depth of penetration of the tools to see beyond the casing. Advances in well diagnostics, particularly in existing infrastructure, are necessary to understand leakage risk and mitigation procedures. Efforts are needed to gather and analyze data on old wells; to find abandoned wells by remote sensing approaches; to quantify the degradation or change in properties of cement, casing, and other well materials; and to simulate well leakage processes.

As a result of their deliberations, these four panels devised the following PRDs:

S-1: Advancing Multiphysics and Multiscale Fluid Flow to Achieve Gt/year Capacity

S-2: Understanding Dynamic Pressure Limits for Gigatonne-scale CO_2 Injection

S-3: Optimizing Injection of CO_2 by Control of the Near-Well Environment

S-4: Developing Smart Convergence Monitoring to Demonstrate Containment and Enable Storage Site Closure

S-5: Realizing Smart Monitoring to Assess Anomalies and Provide Assurance

S-6: Improving Characterization of Fault and Fracture Systems

S-7: Achieving Next-Generation Seismic Risk Forecasting

S-8: Locating, Evaluating, and Remediating Existing and Abandoned Wells

S-9: Establishing, Demonstrating, and Forecasting Well Integrity

4.1 Storage Panel Report: Injectivity and Capacity

Several CO_2 storage projects around the world have demonstrated the feasibility of injecting and storing CO_2 at the million tonne (Mt) per year scale. These include the long-running Sleipner project (Norway), which started in 1996 and has stored ~17 Mt of CO_2 to date, and more recent projects, including the Illinois Basin Decatur Project (USA) and the QUEST project in Alberta (Canada). These projects, along with a wealth of injection experience from the oil and gas industry over decades underpinned by extensive research, provide confidence in the subsurface storage concept intrinsic to CCUS.

The challenge ahead is to ramp up CCUS technology to be able to safely store CO_2 at the gigatonne (Gt) per year scale to meet global CO_2 emissions reductions targets. Although sufficient capacity exists in theory to store CO_2 at the Gt/year scale in the continental and offshore sedimentary basins of North America, Europe, and worldwide, there are many technical challenges that need to be addressed. First, more accurate estimates of storage capacity are needed over large areas (~103–104 km^2) that have been targeted for storage, with associated challenges for site characterization, monitoring, and storage verification. Second, whereas the few current projects are isolated in the given storage reservoirs and often within entire sedimentary basins, injections at the Gt/year scale must involve multiple large-scale projects, potentially within tens of kilometers of one another and accessing similar stratigraphic intervals and probably similar reservoir units. To achieve this degree of scale-up, a better understanding of the permissible pressure increase in these large regions is needed. Pressurization from injection projects is known to extend from 10s to 100s of km from the injection wells, and interference among neighboring projects is inevitable. Thus, there is the need for detailed understanding of the tolerance for pressure rise and potentially the need for pressure management. Furthermore, large-scale projects will require smart methods of controlling and optimizing CO_2 injection, which will involve developing better understanding of the links between small (e.g., subpore and pore scale) and large-scale physical processes in the reservoir.

The key technical issues, questions, and areas in need of better understanding include

- CO_2 migration and trapping processes
- Understanding of when and how caprocks fail
- Physics- and chemistry-based understanding of CO_2 flow at all scales in the reservoir and storage complex
- Impact of flow processes on storage at multiple scales within heterogeneous rock media

In addition to laboratory and field studies, there are many challenges that will require developments in the theory, modeling, and simulation of CO_2 storage processes. The PRDs identified under Storage Injectivity and Capacity will exploit recent advances in the understanding of flow processes and in the use of high-performance computing using large data sets to improve the forecasting of

- CO_2 migration and trapping processes
- Pressurization and dynamic pressure limits
- Reservoir fracturing
- Dynamic geomechanical behavior of rock units

4.1.1 Status of Injectivity and Capacity Technologies

Over the past few decades, a growing set of CCUS projects have steadily tested, demonstrated, and optimized the technologies involved in injecting CO_2 into geological storage units as part of strategies to reduce CO_2 emissions to the atmosphere. CCUS was first implemented at an industrial scale at the Sleipner project (Figure 4.1) in Norway in 1996 [Baklid et al. 1996], and by 2017 there were 21 large-scale CCUS projects in operation or in final stages of development with a collective capacity to capture and store around 40 Mt/year of CO_2 [GCCSI 2016]. This capacity could increase to 100 Mt/year by around 2030, based on CCUS projects currently in the planning stages. However, a ten-fold increase beyond this level would be needed if the greenhouse gas reduction goals embedded in the Paris agreement are to be realized [IEA 2016].

There is therefore a clear need to enable and ramp up the technology required to achieve scale-up from the current capacity level of ~40 Mt/year to the Gt/year level. Current CO_2 storage projects demonstrate that the technology is mature at the level of 1–4 Mt/year per project, but the key challenge is to significantly increase both the number of projects and the capacity per project. The three PRDs under the CO_2 Storage: Injectivity and Capacity theme address the science underpinning the question of how we can achieve storage at the Gt/year level.

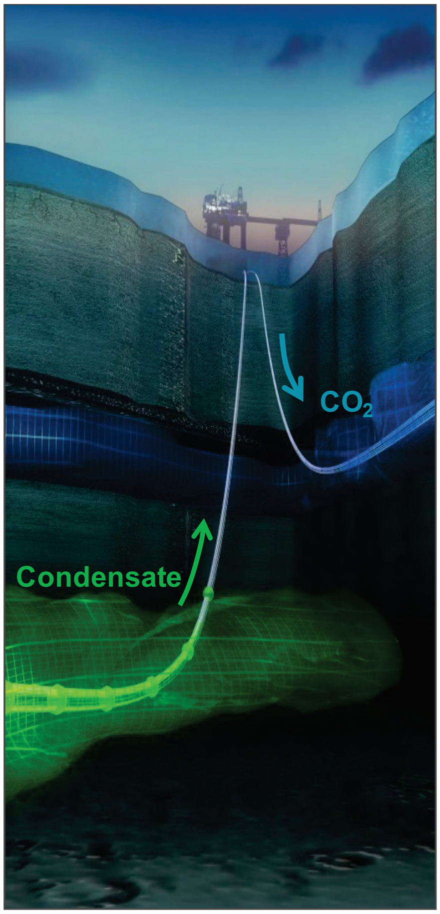

Figure 4.1. The Sleipner CO_2 injection project in Norway. | Image reproduced with permission from Statoil ASA

There are four broad classes of geological storage of CO_2:

1. Storage in deep saline rock formations (saline aquifers)
2. Storage in depleted oil and gas fields
3. Storage as part of enhanced oil recovery projects (CO_2EOR), including in residual oil zones
4. Storage in a more diverse set of rock types, including coal formations, shales, basalts

We focus primarily on storage in saline aquifers and depleted oil and gas fields, as they are expected to have the largest potential for Gt-scale storage, although the concepts will be relevant to all storage options. A key part of the learning process for globally significant scale-up of CO_2 storage has been the insights gained from early-mover projects. This experience has been summarized in various monographs [e.g., Chadwick et al. 2008; Hitchon 2012] and review papers [e.g., Jenkins et al. 2015; Pawar et al. 2015]. To briefly sum up this experience, it is useful to list some key achievements so far:

- Insights regarding how seismic monitoring can be used to monitor saturation and pressure changes associated with the growth of the CO_2 plume, including the use of time-lapse seismic monitoring at the Sleipner [Eiken et al. 2011; Furre et al. 2017], Weyburn [White 2009], and Snøhvit [Grude et al. 2013] projects, as well as continuously active seismic methods at the Frio project [Daley et al. 2007]
- Insights into how downhole pressure monitoring, both within and above the injection interval, can be used to understand the pressure distribution and evolution at storage sites, especially at the Snøhvit project [Hansen et al. 2013] and Illinois Basin Decatur project [Finley 2014]
- Insights into the rock mechanical response to injection, especially at the In Salah [Ringrose et al. 2013; White et al. 2014] and Illinois Basin Decatur projects [Verdon et al. 2011]

- Insights into the complexity of reservoirs and its impact on CO_2 flow paths, plume spreading, and CO_2 storage efficiency—for example, at the Cranfield, Mississippi, project [Hovorka et al. 2013] and the Farnsworth, New Mexico, project [White et al. 2017]
- Insights into optimal monitoring and risk management procedures [e.g., Bourne et al. 2014; Jenkins et al. 2015; Pawar et al. 2015]

Together these projects and studies demonstrate both the technical viability of CO_2 storage and its challenges, while also pointing to the key technologies involved in project execution. This gives us an excellent basis for the research directions identified in this report, focused on the theme of significant scale-up via improved insights from multiphysics analysis of CO_2 storage (Figure 4.2).

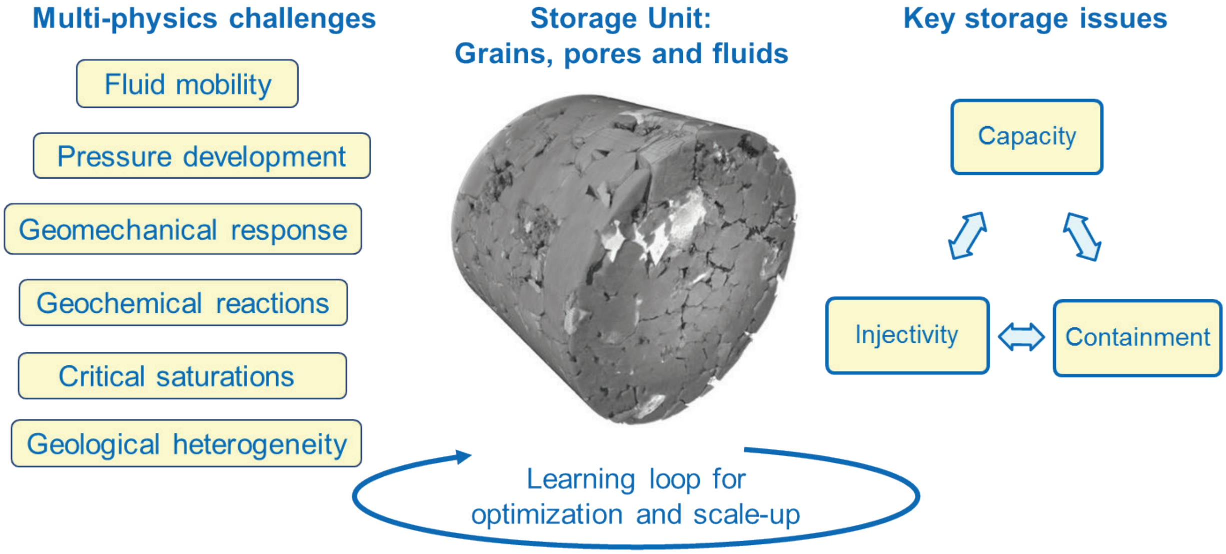

Figure 4.2. Overview of CO_2 storage challenges. | Image courtesy of Sam Krevor, Imperial College London

4.1.2 Scientific Challenges

Advancing multiphysics and multiscale fluid flow

The physics of injection of CO_2 into a subsurface brine-filled aquifer is part of a class of two-phase flow problems. The CO_2-brine fluid pair is usually immiscible, and CO_2 injection mainly follows a drainage process with an unstable mobility ratio. However, as CO_2 migrates in the rock formation, both drainage and imbibition flow cycles may be followed; and a set of geochemical reactions among CO_2, brine, and mineral surfaces will occur. It can be shown analytically [Nordbotten and Celia 2006] that CO_2 in the subsurface typically is distributed with a “curved inverted-cone geometry.”. The detailed shape of the CO_2 plume, and therefore the efficiency of the process, is strongly controlled by the fluid mobility, the viscous/gravity ratio, and the geological architecture [Nordbotten and Celia 2006] (Figure 4.3).

For any particular case, a storage capacity coefficient C_c can be calculated, where C_c is the ratio of the volume of CO_2 injected to the available pore volume, V_{PV}. For an analytical case, C_c is given by

$$C_c = \frac{V_{injected}}{V_{PV}} = \frac{Q_{well}\, t}{\phi B \pi (r_{\max})^2},$$

where Q_{well} is the injection rate over a time interval t into a horizontal infinite saline aquifer unit with thickness B and porosity ϕ, and r_{max} is the extent of the expanding plume. It is assumed that there is a hydraulically connected pore volume beyond the area covered by the plume (i.e., for $r > r_{max}$) to absorb the pressure increase induced by the injection of the volume of CO_2.

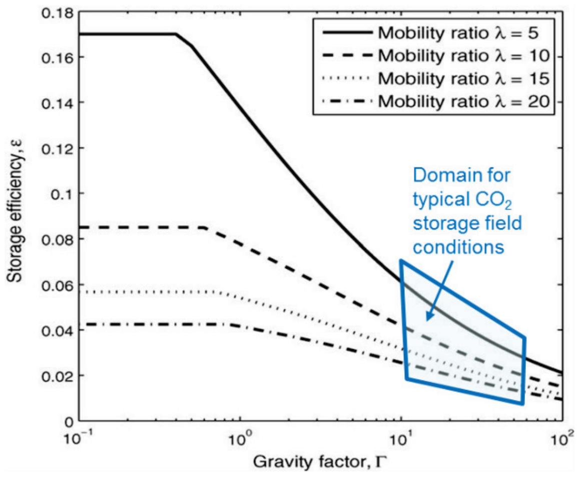

Figure 4.3. Storage efficiency, ε, as a function of the gravity factor Γ for an analytical case. | Image redrawn from Okwen et al., "Analytical solution for estimating storage efficiency of geologic sequestration of CO_2" *Int. J. Greenh. Gas Con.* **4**, 102–107, Copyright 2010 with permission from Elsevier

For a viscous-dominated case, around 25% of the storage volume could in theory be used (in the absence of pressure constraints). However, the effects of fluid buoyancy (gravity forces) reduce the actual efficiency to a general range of 1–6% (Figure 4.3; [Okwen et al. 2010]). Time-lapse seismic imaging data at the Sleipner CO_2 injection project ([Arts et al. 2008; Furre et al. 2015]; Figure 4.4) allow imaging of the spatial distribution of the CO_2 plume. Using these data, Eiken et al. [2011] estimate the fraction of the pore space used at the Sleipner site to be around 5%. The presence of multiple shale layers in the Utsira sandstone formation has caused additional spreading and trapping of CO_2 at the site, to give a storage efficiency that is higher than would have occurred in a homogeneous sandstone. Near-well storage efficiencies are therefore controlled by the interaction of the fluid migration process (flow physics) with the geological architecture (reservoir heterogeneity).

Similar interactions between heterogeneities and fluid forces will control how fast and how far CO_2 will migrate when it flows outside of a structural closure. Forecasting this long-term migration is critical to large-scale CO_2 storage deployment to avoid interferences with other subsurface resources and to limit monitoring costs.

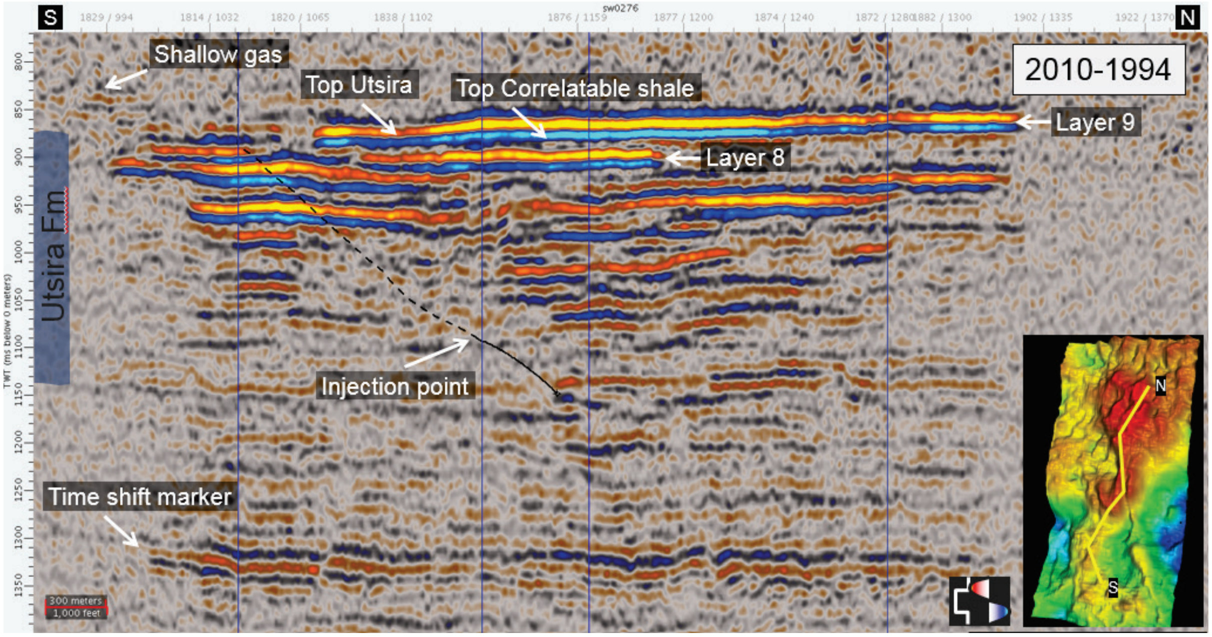

Figure 4.4. Sleipner time-lapse seismic data, showing amplitude difference between 2010 and 1994 surveys. Bright amplitudes reveal the presence of CO_2 complicated by the effects of time shifts and thin layer effects. | Image courtesy of Statoil ASA

In addition to the physical processes controlling CO_2 as a mobile phase, other important processes and trapping mechanisms involved are residual trapping, solubility trapping, and mineral trapping. These CO_2 trapping mechanisms will work over time to increase storage security in the long term. However, there remains considerable uncertainty around quantifying the efficacy of each process for any particular site, and lack of knowledge regarding how to optimize injection strategies to make the best use of the available pore space.

This leads us to the essential motivation for PRD 1, Advancing Multiphysics and Multiscale Fluid Flow to Achieve Gt/year Capacity: How can we better quantify and optimize CO_2 storage efficiency around the injectors?

More specific goals of this research objective are to

- Evaluate the contributions of different physical processes in controlling near-well CO_2 storage efficiency
- Consider these multiple physical processes across the multiple scales that control the fluid dynamical processes
- Research ways in which knowledge of fluid dynamical processes can be used to optimize storage at a given site based on detailed multiscale geological architecture

For further explanation of these research goals, refer to PRD S-1.

Understanding dynamic pressure limits

Alongside the issues of fluid mobility and CO_2 trapping processes involved in storage is the coupled problem of pressure and geomechanics. As CO_2 is injected into the subsurface, some degree of pressure elevation over the background pressure will occur. This pressurization effect has been modeled by analyzing end-member geological boundary conditions, which Zhou et al. [2008] summarize in terms of three main systems (Figure 4.5a). An open storage system has a very large connected aquifer around the storage site, meaning that only limited pressure buildup occurs. In contrast, a closed system (such as a storage site bounded by sealing faults) will have very strong pressure constraints leading to very limited storage capacity. Semi-closed systems represent a fairly common hybrid case in which various partial permeability barriers are found around a storage unit, potentially limiting storage capacity but allowing some pressure dissipation to occur. Note that brine displacement into neighboring formations will lead to pressure increases in these formations, which may also affect (decrease) their capacity to store CO_2. Real 3D geometries of geologic storage systems are complex and more likely to fall into the semi-open or semi-closed categories (Figure 4.5b) requiring advanced site characterization and modeling studies.

At the basin scale, all formations are in contact with other formations or hydrogeological units, which can be partly open toward the surface or seabed outcrop. Ensuring successful containment of stored CO_2 thus requires assessment of complex geological systems (the storage complex). Whatever the degree of hydrological communication between rock units, significant pressure rises are expected in the injection area for Gt-scale storage; these must be understood and managed.

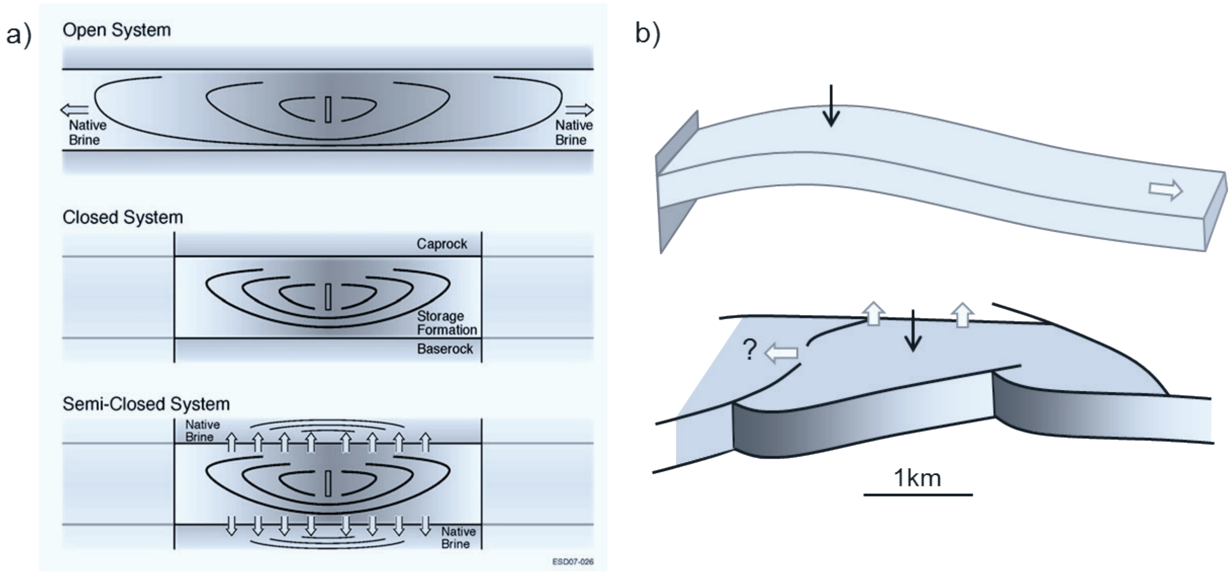

Figure 4.5. (a) Open, closed, or semi-closed systems. (b) Typical 3D geometries of semi-open and semi-closed geologic storage systems. | (a) Image reproduced from Zhou et al., "A method for quick assessment of CO_2 storage capacity in closed and semi-closed saline formations," *Int. J. Greenh. Gas Con.* **2**(4), 626–639. Copyright 2008, with permission from Elsevier. (b) Image courtesy of Philip Ringrose

Various approaches have been proposed for managing or limiting pressure buildup in CO_2 storage projects; and with scale-up to the Gt/year scale, these pressure management solutions will become critical. Pressure management for CO_2 storage includes the following options:

- Improved understanding of the detailed nature of the geomechanical limits that control the maximum allowable injection pressure [e.g., Streit and Hillis 2004; Rutqvist 2012; Bohloli et al. 2017]
- Optimal use of pressure depletion from gas field production to improve subsequent storage project capacity [e.g., Clarke et al. 2017]
- Regional analysis of pressure buildup related to multiple CO_2 injection projects [e.g., Gasda et al. 2017]
- Brine production to compensate for CO2 injection [e.g., Birkholzer et al. 2012]
- Use of novel well solutions to distribute pressure associated with injection [e.g., Nazarian et al. 2013]

The need to understand and control the pressure and geomechanical responses to CO_2 injection points to the essential motivation for PRD 2, Dynamic Pressure Limits for Gigatonne-scale CO_2 Injection:

What are the allowable pressure limits for CO_2 injection projects?

More specific goals of this research objective are to

- Identify and quantify the hydrologic and geomechanical hazards during pressurization
- Improve quantification of the allowable and acceptable reservoir- and basin-scale pressure rises for dynamic CO_2 injection processes
- Improve the understanding of cap-rock and reservoir hydraulic fracturing or fault-slip mechanisms

For further discussion of these research goals, refer to PRD S-2, Understanding Dynamic Pressure Limits for Gigatonne-scale CO_2 Injection.

Optimal injection and the near-well environment

Injectivity requirements for Gt-scale injection at multiple sites provide strong motivation to control injectivity and avoid the need for excessive numbers of expensive injection wells. Various processes, such as solids precipitation and formation damage, can decrease injectivity, whereas near-well fracturing and other treatments can enhance injectivity. Fracturing by coupled thermal and hydraulic means is potentially feasible because thermal fractures probably will not threaten cap-rock integrity but rather will remain close to the injection well. Approaches are needed to avoid formation damage and solids precipitation, which may decrease injectivity in the near-well region depending on the composition of the CO_2 injection stream and the local reservoir geochemistry.

Long experience from the oil and gas industry and existing CO_2 injection projects [e.g., Brock and Bryan 1989; McMillan et al. 2008; Burton et al. 2009] provide a foundation upon which to build a focused research program for optimal injectivity. The approaches available to improve the understanding of induced fractures (hydraulic and thermal) and other near-well treatments to enhance injectivity drawn upon combined laboratory, theoretical, and field research, including utilization of underground laboratories. In this area, it is critical to know whether it is possible to develop CO_2-specific additives that can help manage injectivity, and whether there is feasible next-generation well technology that can be used to manage injectivity.

The potential for significant developments in optimizing injection give us the overall motivation for PRD S-3, Optimal Injection of CO_2 by Control of the Near-well Environment:

> To optimize CO_2 injectivity by understanding fracturing mechanisms, using near-well treatments, and deploying next-generation well technology

These and other research challenges are outlined in PRD S-3.

4.1.3 Why Now?

In addition to the growing urgency for taking action as soon as possible to reduce greenhouse gas emissions at the levels needed to put off the worst effects of climate change, there are several reasons that the research outlined by the Storage Injectivity and Capacity panel will be successful and should be initiated now. First, the recent and ongoing CO_2 injection projects have provided the experience and data that reveal simultaneously the promise of CCUS and the associated challenges. On the positive side, the Sleipner and Illinois Basin Decatur Projects show that single-well injections at the Mt/year scale can be carried out safely. Challenges related to injectivity were experienced early in the Snøvhit project, but they were solved by establishing an alternative injection zone. Challenges related to over-pressure were experienced in the In Salah project, resulting in cessation of injection after several years as a matter of caution. These projects highlighted the need for careful consideration and design to ensure injectivity and avoid hydraulic fracturing by over-pressurization of reservoirs. Looking to the urgent need for Gt-scale CO_2 injection, and notwithstanding the ability to scale up injection by simply increasing the number of wells, injectivity and capacity requirements become significantly larger relative to existing CO_2 storage projects.

In addition to the experience from field projects, the second reason that a new emphasis on injectivity and capacity research is timely is that the worldwide research community has developed significant new knowledge and capabilities over the last decade and a half of focused CCUS research. For example, important research in pore-scale multiphase flow and transport processes [e.g., Reynolds et al. 2017] has begun to illuminate the CO_2 flow dynamics and its representation as relative permeability functions (including hysteresis effects). However, advances are needed in this area to expand the scales of investigation downward to include intragrain porosity and surface reactions, and upward to include sedimentary structures and fault and fracture flow. Synchrotron imaging, focused ion beam, x-ray computerized tomography, and other imaging techniques have been developed and demonstrated to provide the kinds of imaging needed to improve understanding of CO_2 flow and reaction processes in the pore space [e.g., Silin et al. 2011; Kneafsey et al. 2013]. At the same time, advanced computing capabilities make it possible to simulate fluid flow (e.g., non-Darcy Stokes flow) and reaction at micron scales using 200 million grid blocks (Figure 4.6) [Molins et al. 2014; Trebotich et al. 2014].

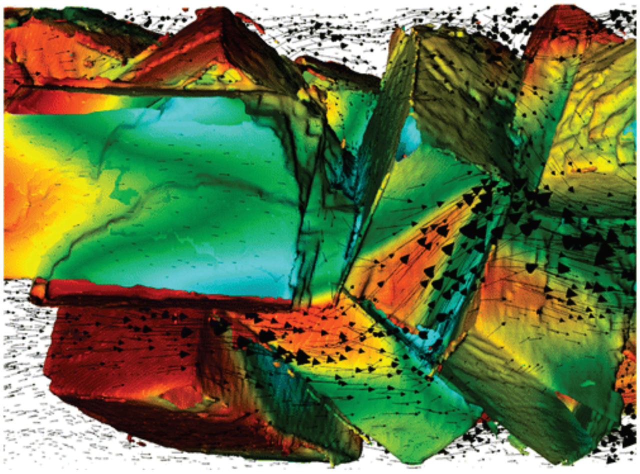

Figure 4.6. Calcite grains imaged at the micron scale using the Advanced Light Source at Lawrence Berkeley National Laboratory are also discretized at the micron scale for numerical simulation of flow and reaction. Simulated calcite concentration is shown by the rainbow shading, and simulated CO_2-saturated water flow is shown by the vectors. | Reprinted from Molins et al. 2014. *Environ. Sci. Tech.* **48**(13), 7453–7460. Copyright 2014 American Chemical Society

High-performance computing (HPC) simulation capabilities have also been demonstrated for geologic carbon sequestration and other relevant processes on the reservoir scale [e.g., Yamamoto et al. 2014; Hammond et al. 2014]. Not only do the advances in massively parallel computing allow higher resolution of large domains so that heterogeneity and fluid-phase saturations at relevant scales can be modeled, but HPC also allows more accurate modeling of coupled processes and different physics in different regions. For example, the large pressures generated by Gt/year–scale injection of CO_2 cause changes in the stress field that manifest as geomechanical deformations, including fracturing and fault-slip. At the same time, changes in composition of the fluid caused by CO_2 injection drive geochemical reactions. In these cases, coupled hydro-mechanical-chemical processes need to be simulated. In addition, flow or other processes in different regions of the domain may be governed by different physics and therefore described by different mathematical models. One example is that the flow in the well needs to be described by the Navier-Stokes equations for viscous flow, while flow in the reservoir can usually be described by Darcy's law. In computing a coupled well-reservoir system, we need to solve the coupled well-reservoir equations [e.g., Pan and Oldenburg 2014]. Recent advances in handling and analyzing large data sets and in the use of pattern recognition algorithms allow further possibilities for making advances toward safe and efficient Gt-scale CO_2 injection.

4.2 Storage Panel Report: Monitoring, Verification, and Performance Metrics

Research undertaken over more than two decades has demonstrated the efficacy of monitoring technologies in tracking the evolution of injected CO_2 and in establishing the safe operation of geologic CO_2 storage sites [Chadwick et al. 2012; DOE 2012; Jenkins et al. 2015]. Most regulations require some form of monitoring to ascertain the safe behavior of the injected CO_2 during the injection phase [EPA 2016; Dixon et al. 2015] and particularly to establish that future behavior will continue to contain the CO_2 within the target geological structures and prevent any leakage to protected domains such as groundwater, soils, seawater, or the atmosphere [Blackford et al. 2015; Dixon and Romanak 2015].

Many technologies have been applied in CO_2 storage projects, both conventional technologies developed in other industries, notably but not exclusively the oil and gas industry, and new technologies that are now being adapted and developed. The International Energy Agency's (IEA) Greenhouse Gas R&D Programme online monitoring selection tool provides a useful summary of these technologies and provides some practical examples of their deployment in mainly research-scale pilot injection projects.[1]

Insights gained from storage pilots have provided a better understanding of the practical approaches to select, integrate, and deploy technologies to address the site- and project-specific monitoring requirements. Furthermore, technological advances present CO_2 storage operators with new opportunities to further improve capabilities to directly detect and measure the processes associated with CO_2 injection.

4.2.1 Scientific Challenges

The IEA estimates that a total of 94 gigatonnes of CO_2 will need to be captured and stored by 2050 to meet the 2° scenario [McCulloch 2016]. Meeting these targets will require the injection of 100s of million tonnes per year at many sites over several decades. Scaling up the rates and number of injection sites from current pilot scales to meet this climate target presents a number of opportunities to improve and develop new monitoring technologies. In some regions, sites will be required to operate in proximity to one another, creating potentially large volumes that must be monitored (tens of cubic kilometers). The research areas for the Monitoring, Verification, and Performance panel were therefore developed in the context of moving from a small number of intensively monitored mainly pilot and demonstration projects to full-scale gigatonne storage that will be operated commercially and will require fit-for-purpose monitoring programs.

The first research area identifies scientific challenges and proposes research that addresses the need to more directly detect and measure CO_2 in deep formations. There are a number of drivers for this requirement; but in summary there is a need to demonstrate, during operation, that a storage site is behaving as expected and that long-term geological containment is being achieved. Monitoring provides the information that establishes the convergence between actual site behavior and simulations of behavior over the long term: a fundamental requirement to enable site operators to close a site and transfer long-term liability back to national authorities. The second research area identifies challenges of identifying and monitoring deviations from predicted behavior that could result in material impacts, and monitoring the efficacy of planned and unplanned mitigation and remediation responses to the deviation. Although it focuses somewhat on the causes and impacts of leakage, these anomalies also include events that do not pose a threat of leakage but may also lead to changes in operation.

4.2.2 Monitoring to Demonstrate Containment and Enable Storage Site Closure

Transforming far-field monitoring with new tools to directly measure state variables

Many tools are currently available to monitor so-called state variables of primary importance to CO_2 storage projects. These variables include but are not limited to pressure, temperature, chemistry, density, stress, strain (deformation), and fluid saturation. Monitoring tools and techniques have been developed

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[1] http://www.ieaghg.org/ccs-resources/monitoring-selection-tool

either in other disciplines, such as the oil and gas or geotechnical industries, or as fit-for-purpose techniques from small- to large-scale demonstration or commercial projects (Figure 4.7).

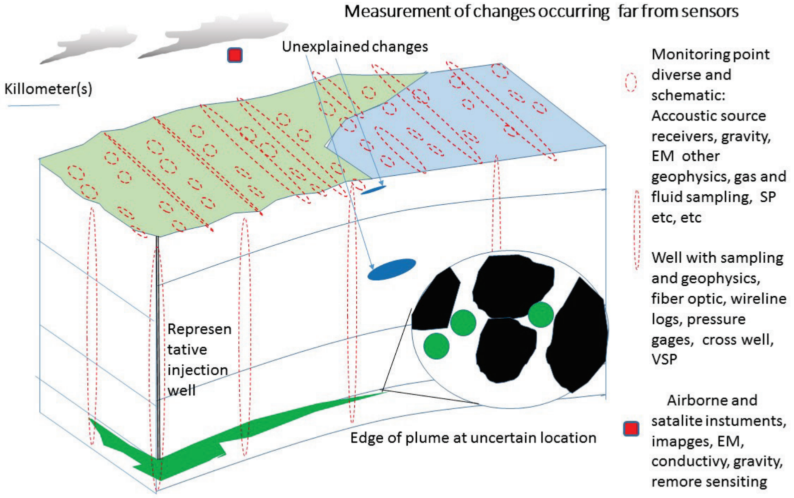


Figure 4.7. A schematic view of monitoring of geological CO_2 storage. | Image courtesy of Susan Hovorka, Gulf Coast Carbon Center, University of Texas–Austin

Four broad challenges with regard to current monitoring tools have been identified. (1) Many of the current monitoring tools deployed in the storage projects are indirect methods, which do not directly measure a primary state variable such as pressure or fluid saturation but rather measure parameters that give an indirect indication of site behavior. The state variables must be interpreted from the indirect monitoring techniques or converted from geophysical parameters based on rock physical models. (2) Direct measurements of state variables are limited to point measurements either from well-based monitoring in the storage complex or at fixed locations above a storage site. These have many limitations, including cost, choice of location, robustness, and maintenance requirements; and they can create containment risks because each well penetration of the confining layer increases the risk of leakage. (3) There is no scientific consensus on how to scale up current monitoring techniques to the gigatonne scale. (4) All of these monitoring techniques add cost. Worldwide implementation of geological CO_2 storage must be as low in cost as possible.

New tools are needed for direct observation of state variables. Ideally, these tools will accomplish the following:

- Directly measure one or more of the state variables of the system (e.g., pressure, temperature, fluid saturation, fluid chemistry, stress, strain/deformation, density, pH, fluid viscosity).
- Provide their measurements temporally and/or spatially. For example, over a range from discrete measurements at a point in space or time, all the way to continuous measurements in time over large spatial domains (e.g., fiber-optic sensors).
- Offer improved parameter resolution and reliability compared with what is currently available.
- Offer improved reliability over the tools currently available. For example, currently a down-hole pressure sensor failure requires a costly tubing-string removal/replacement, and a fixed-gauge failure in a monitoring well is unrecoverable.
- Provide information at increased distances away from the storage complex access points, such as injection or monitoring wells. Ideal new tools would provide information on state variables in remote locations in the storage complex. In the future, a next-generation tool would provide state variables from the injection wellbore to the CO_2 plume or pressure front.
- Complement and/or enhance existing indirect measurements (e.g., seismic, interferometric synthetic-aperture radar, and resistivity).

Smart monitoring in the far-field

CO_2 storage projects require monitoring operations at the site to understand the behavior (location, attribution, and quantification) of the CO_2 plume, including the assurance that leakage of the CO_2 has not occurred. Monitoring programs may require measurements of the CO_2 plume behavior with wide spatial coverage, good spatial resolution, and high temporal frequency, and subsequently may require regular or continuous monitoring. Monitoring programs that rely largely on repetitive, surface-based surveillance may be costly, be limited in resolution, and face logistical and societal obstacles in some circumstances.

There is therefore a need to develop and validate novel methods of deploying monitoring tools for direct measurement (e.g., downhole equipment in wellbores) and indirect measurement (e.g., surface geophysics, satellite imagery) to better define (locate, attribute, and quantify) the outer extent of a CO_2 plume in far-field. The highest accuracy of monitoring techniques is only within the direct vicinity of the wellbore, which must be extended into the far-field reservoir. Subsurface tool deployment requires costly drilling. For example, although 4D vertical seismic profile data are sufficient to monitor the plume, monitoring of a larger area requires multiple deep wells. Lower-cost drilling technologies and reductions in the density of tool deployment are needed. Tools are large, and multiple tools in wellbores are difficult to deploy and prone to fail. Reductions in tool scale and improvements in tool reliability are paramount. Although buried geophone arrays provide the highest resolution for 4D seismic acquisition, and reduce the need for repeated land access, they still require land access for a densely distributed grid of geophones. Thus, improvements in the sensitivity of geophones to reduce numbers are also required.

Reaching into the far-field requires either (1) downhole tools deployed in deep boreholes that interrogate from underneath the plume (e.g., Muon detectors) or at similar depth levels laterally into or above the reservoir (e.g., pressure gauges, fiber optics inside and outside casings, conventional geophones) or (2) tools deployed in shallow boreholes interrogating vertically above the area of interest. To improve tool deployment, devices first must be further optimized and miniaturized. They also must deliver incremental and transformational changes in drilling technology for both onshore and offshore sites, including reductions in environmental impact and cost.

A step change in drilling technology is required to provide faster, cheaper, and safer drilling; quicker mobilization/demobilization; better wellbore stability; and less environmentally intrusive setup of the drill pad. Step changes in drilling technology could be achieved by developing new drilling rigs (e.g., improved coiled tubing rigs with full steering and sensing capability, improved methods to drill deep and directional micro-boreholes, improved bit designs for full-face drilling, improved drilling rates via improved monitoring of and responsiveness to bit wear, and light and durable carbon fiber drill rods.

Permanently deployed smart sensors should provide higher data quality, provide repeatable acquisition, allow real-time data processing, reduce acquisition time, and reduce the impact on landowners and industries. Device optimization and miniaturization can be achieved, for instance, by furthering research on distributed acoustic sensors (on fiber optic cables), which have the potential to measure many variable state parameters, such as pressure, temperature, strain and chemistry, while being durable and easy to deploy.

Improving methodologies for monitoring plans

Current guidelines for monitoring CO_2 storage projects do not provide guidance regarding the level of detail needed to provide safe, secure CO_2 storage. Operational storage projects are of a first-of-a-kind nature and tend to have monitoring programs that collect large amounts of data to serve scientific purposes. In contrast, future large-scale CO_2 storage projects will require fit-for-purpose, cost-efficient monitoring systems. There is currently no consensus on the definition of "fit-for-purpose," as the monitoring requirements depend on the regulatory regime; some regulations appear to require detailed and extensive monitoring programs, creating barriers for potential CO_2 storage operators. A mature assessment of parsimonious but sufficient monitoring plans has not reached wide acceptance; it would require assessments of the types of monitoring tools and analysis needed, the frequency and density of measurements, and how many data are sufficient.

A fit-for-purpose monitoring system produces the evidence that the CO_2 storage system is behaving as expected. The monitoring system design should be risk-based, i.e., focused on the elements that are considered to have the highest risks of anomalous behavior. The challenge is to be able to develop a methodology that demonstrates the ability of a monitoring system to define the state of the storage system. The methodology should assess the value of the individual monitoring techniques in reducing the uncertainty in site performance. A fit-for-purpose monitoring system contains those monitoring techniques that, together, produce the evidence for system performance with an acceptable degree of uncertainty. A key low-Technology Readiness Level goal for monitoring is to validate models that describe how buoyant CO_2 plumes will migrate at the end of injection—knowledge required to document CO_2 plume stabilization to enable site closure.

Methodologies should be able to optimize the location of individual sensors within potentially integrated sensor networks. The methodology must enable robust, systematic assessments to show how the addition of a monitoring technique decreases the uncertainty in reaching conclusions regarding site performance. A metric for the performance of the storage system should be developed which can be seen as a measure of the extent of the difference between observed and measured monitoring data, or between the expected behavior of the CO_2 and that obtained from inverting the monitoring data. The value of a monitoring technique lies in its ability to decrease the uncertainty regarding the value of the site performance metric.

Model validation is needed to test the extent to which a model calibrated during injection is sufficient to forecast plume stabilization over the range of rock types, fluid types, and storage compartment geometries. Validation requires laboratory analysis of rocks and fluid, physical models, and scaled field experiments. A successful outcome will reduce uncertainty and target the monitoring needs. There is a need to improve upscaling in the time domain (i.e., over longer time periods). Uncertainties that cannot be satisfactorily reduced before a project starts or in the early stages of the project will require a monitoring program deployed at the end of injection to make needed measurements as stabilization occurs. This approach will lead to a sharper, more targeted set of uncertainties, which will allow tailoring of a set of monitoring tools and approaches needed to ensure that closure targets are met.

Improving interpretation and use of large, complex data sets

Rapid advancements in sensor technology over the last 20 years have provided high-volume and more complex data sets requiring interpretation. However, traditional interpretation techniques involve significant human expertise and currently include only basic automation and analytics. Significant time is therefore required for human deliberation to resolve information gained from discrete, imprecise, conflicting, or incomplete data sources. Hence, these techniques are limited by the available human capability and/or processing power. There is therefore a gap in the existing capabilities to consistently and systematically use all the data now being collected to the maximum extent to extract meaningful information and enable better decision making.

To aid decision making, insights should be extracted from large data volumes associated with storage projects, using advanced data mining, analysis, and integration to create data flows and automatically actionable decisions. Algorithms and hardware should be improved through techniques such as pattern recognition algorithms and machine learning so that they can identify trends from a variety of data sources that are linked with advanced control systems and predictive fault detection and prediction software. Artificial intelligence and cognitive computing can enable human reasoning capabilities to solve interpretation problems faster and with higher accuracy. Stress-testing of reservoirs via multiple realizations is needed to test the full range of uncertainty associated with multiple data sources and to examine the full range of outcomes and their consequences.

Interpretations of individual data sets often result in non-unique solutions. To overcome this issue, joint inversion of, for example, gravity, electromagnetic (EM), and seismic data represents a powerful tool to detect the evolution of the CO_2–water front. As electrical resistivity is sensitive to saturation, it may be advantageous to jointly invert gravity and EM data using seismic data; and this approach could be extended to include self-potential data. Moreover, the joint inversion of geophysical data and subsequent interpretation of the inverted response are prone to problems if the physics of the process is not taken into account. Research is needed to advance methodologies (tool selection, data integration, and interpretation) to enable improved interpretations that lead to significantly reduced uncertainty. Accomplishing these improvements will require fully coupled inversion of geophysical data, the physics of the process, and reservoir textural and structural information.

Assessing anomalies and providing assurance

Anomalies arise when data of any type (e.g., seismic, pressure, geochemical), measured inside or outside the storage reservoir, indicate abnormalities, irregularities, or deviations from the predicted data range. Anomalies indicate that the system behavior could lead to material impacts. Thus, monitoring for such anomalies requires a robust methodology that is able to quickly identify when an acceptable threshold has been exceeded, which may trigger further action to assess or attribute the source of the variation. Four specific research priorities have been identified that will improve capabilities for assurance monitoring.

New and improved methods of location, attribution, and quantification

For assurance monitoring, anomalies must be detected and located and their sources must be attributed to determine if the anomalous signal results from storage operations or some other industrial or environmental cause. A closely related goal is a need for methodologies that are simple enough to be understood by lay stakeholders and easily implemented, perhaps even by stakeholders or the public themselves. When an anomaly is attributed to storage operations, further (pre-) defined action may be taken [Dixon and Romanak 2015]. Certainly, any emissions related to storage that reach the atmosphere or seabed will need to be quantified for accounting purposes. Similarly, if claims of environmental damage or public concerns about containment arise, methods will be needed to quickly and accurately assess anomalies reported by stakeholders to either address public anxiety or act quickly to mitigate environmental damage and/or account for the loss.

Many methods are available for implementing the various components of assurance monitoring, but not many have not been validated because there is a lack of experience with loss of containment. For anomaly location, shallow controlled-release experiments suggest that the ability to accurately predict where an anomaly will occur at the surface needs further improvement, because at this time the needed parameters cannot be gathered within heterogeneous, thick geologic overburden to adequately predict the fate of transport of CO_2.

Methodologies for location, attribution, and quantification will rely heavily on the tools available for their implementation. Thus advances in methods, tools, and technologies must develop simultaneously to optimize the design and implementation of monitoring systems. A major requirement will be continuous data collection with integrated data analysis and with remote user-friendly interfaces. For example, autonomous capabilities for optical, laser, and spectroscopic methods are needed.

For source attribution, variability is a major issue to be addressed. We now know that environments are rapidly changing as shifts in land-use, population growth ,and climate change itself accelerate. Baseline-dependent methods, especially in the nearest-surface environments where variability is highest, are likely to create false positives for leakage—as was the case, for example, in the Kerr Farm incident at Weyburn and at the Tomakomai project [Romanak et al. 2014; Uchimoto et al. 2017]. Baseline-independent methodologies, such as stoichiometric process-based approaches in both terrestrial and marine environments, should be advanced. Methods that use tracers in new and innovative ways are also of interest. New and improved tools are needed—including economical field-based N_2 sensors, and sensors for pressure, temperature, and chemistry (e.g., hydrocarbons, dissolved inorganic carbon, and pH)—especially for advanced marine sensing techniques such as acoustic bubble detection. Sensors must be durable and retain their accuracy and precision in harsh environments and/or over long time frames.

These include multi-level pressure sensors with life-long reliability and sensors to monitor wellbore integrity issues such as corrosion and leakage.

Risk-based techniques and methodologies for assessing the value of anomaly monitoring to design monitoring programs

Risk assessment and management represent critical elements in developing a CO_2 storage site and ensuring its viability throughout the project lifetime. They inform the selection of an appropriate storage site—establishing the requirements for project viability in the initial phases—and subsequently enable the development process to mitigate possible events and to plan appropriate surveillance with considered intervention options. Effective communication tools are needed that capture the complexities and uncertainties of the site to the satisfaction of regulators, investors, operators, and the public. Risk assessment methodologies are generally classified in two main groups: qualitative and quantitative.

An important approach for integrity risk management is to assess the temporal change in storage risk across a defined risk period within the lifetime of the storage project: to understand not only *what* the integrity risks are but also *when in time* these risks are increasing/decreasing and *where in the volume* each risk may occur. This approach provides the opportunity to make responsible and cost-based project decisions. Temporal risk assessment is a key component in successful CO_2 storage projects, supporting decisions in the present for future possible events. The quantitative risk assessment approach integrates dynamic simulation and quantitative risk assessment data to consider where the risk events are, relative to the location and mass of the injected CO_2. The analysis also considers the effects of changing pressures and other features of the migrating CO_2 plume. It provides a series of outputs that can be used to assist in risk management, decision support, injection planning, and performance prediction.

Research is therefore needed to enable the potential value of a wide range of monitoring technologies to be evaluated against their capabilities to reduce risk and uncertainty. Improved risk-based methodologies should be developed that allow the creation of fit-for-purpose, integrated, robust, autonomous monitoring systems for assurance monitoring.

Staged monitoring programs and workflows

Monitoring to detect anomalies is relatively mature and well-developed, as is evidenced by the now-routine development of ideal and prototype monitoring plans and existing regulatory requirements. This experience has come both from controlled-release experiments in which anomalies are created and from successful field deployments. Dozens of controlled release experiments have tested the methods at different release rates and in various settings, and more are in planning. Extensive experience with successful (nonleaking) field projects has provided opportunities for public engagement around project development. But a lack of experience with actual releases from real storage projects indicates the need for better ways of dealing with concerns or allegations of harmful anomalous conditions. All of these experiences provide background and illuminate needs for gap-filling workflows to rapidly respond to incidents and anomalies.

A staged workflow has within it a decision tree; an event has a response—e.g., to collect and analyze data—and the outcome of that analysis leads to a recommendation. Recommendations might be (1) to start a mitigation process, (2) to report that no material impact to the project has occurred, or (3) to collect additional data.

A refined workflow is needed to create a technically grounded, widely accepted and understood sequence of technical responses that are triggered by the identification of an anomaly. This response must be staged so that the response is neither sluggish (exposing the project to site damage, loss of stored CO_2, and reputational loss) nor overly vigorous.

As wide agreement on best practices or protocols does not exist, there is a need to create a workflow that is applicable to

- Different stages of a project
- Anomaly location in all domains
- The location and characteristics of site
- The level of risk—types of receptors, consequence
- Clarity of the signal—should the project respond immediately, and what level of additional assessment is needed

The ideal staged workflow would be developed as part of the pre-injection planning and then updated in response to improvements in characterization made during operational monitoring and model validation. Seeking methods that are efficient and effective in keeping the response plans evergreen is important. A key gap is that, although unacceptable and impactful events will not occur at well-selected and properly operated sites, the project must be ready to respond to an anomaly, assess it, and then mitigate and remediate it. The project must be equally ready to respond if a change in the geosystem indicates damage, but turns out to be an error in measurement or interpretation and not related to the injection project. The diversity of incident types will pose challenges that must be addressed.

The types of incidents that will occur, and whether they are material to a project, will vary depending on the site and the recipient characteristics. The workflow is also likely to evolve over the life of the project. However, once a set of anomaly (or alleged anomaly) response workflows have been developed and tested, the design task will become easier. Development and testing of a portfolio of approaches is a research priority. The program should develop concepts, models and controlled anomalies to test and demonstrate the usefulness of the workflow.

Smart monitoring systems

Many mature tools have been deployed at demonstration sites internationally. Technology transfer from other industries, notably the oil and gas industry, has been successfully used in monitoring CO_2 storage at a medium scale for decades; and technologies are continuously developed in those other industries. However, the unique characteristics of CO_2 storage and the spatial scale of gigatonne deployment require new and innovative ways of developing smart monitoring systems.

The science challenges lie in the need to develop and test the integration of multiple tools, necessary for monitoring state parameters, in new environments to meet new requirements. These requirements include a monitoring system that is scalable and that can provide continuous real-time data autonomously. Such systems should be capable of reacting to changing parameters to provide more intelligent and appropriate data (e.g., increased sampling frequency or additional parameter measurement).

Research is needed to develop intelligent integrated monitoring systems that can be, to varying degrees, autonomous and/or remotely operated, thereby reducing the costs of data collection. Furthermore, advanced algorithms are needed that can autonomously differentiate anomalous changes in site performance that might lead to material impacts, from other changes that are either not anomalous or not likely to lead to material impacts. These systems must be robust and capable of performing in harsh environments (e.g., at elevated temperatures and pressures in corrosive environments) such as wellbores or in offshore environments.

4.2.3 Why Now?

There is a practical need for direct measurements of state variables to calibrate geological models and to verify convergence of observed with simulated site behavior, which drives the scientific development of new technologies for measuring the state of the subsurface and surface domains (geosphere, hydrosphere, atmosphere, or seafloor). Promising examples include nanoparticles, optical fiber technologies, remote sensing technologies and autonomous monitoring platforms (e.g., Autonomous Underwater Vehicles and Unmanned Airborne Vehicles). Recent shifts in focus by public and regulators, as well as approaching commercialization, have increased concern that storage projects attain long-term benefit, and do not evolve to become problems. Experience from small-scale projects with closure is limited and may not be sufficient to provide needed certainty. Advancements in big data handling, algorithm development and analytics, and low-cost high-powered computing have created an opportunity to augment conventional human based interpretation practices, and the opportunity to extract more insights and enhance decision making.

Although there is valuable experience from demonstration sites in varying sizes, in scaling up we will need to have robust and defendable processes that capture complexity, but are amenable to group communication to project teams, and lead to the identification and targeting of potential anomalous events. Experience has informed the problem of designing a responsive workflow, tested and validated a number of tools, and highlighted the need for tool improvement under much of the spectrum of relevant site conditions and incident types. In addition, workflows from other related domains such as oil and gas operation, geothermal operations, and other civil engineering problems can be applied to storage problems. To be used effectively, new tools and approaches require incorporation into a workflow.

Advances in materials and sensors; in communications technology, especially wireless telemetry from remote locations; and in the management and interpretation of large datasets being undertaken in other communities allow the integration and development of “smart” monitoring systems to be initiated. Accurate, quick, and sure methods are sorely needed to protect projects and the environment. Because quantification is in essence an activity that combines both location and attribution, our ability to quantify “emissions apart from natural baseline” as many regulations require is currently behind the research curve. The staged workflow includes location of an anomaly, attribution of the source of the anomaly, and then quantification of the anomaly. Demonstration of absence of anomalies is a condition for showing that the site can be closed.

4.2.4 Conclusions

The impact of newly-developed smart convergence monitoring to demonstrate containment and enable storage site closure will enable the deployment of gigatonne storage projects. It will assist with public acceptance (i.e., enabling operators to gain their social license to operate) and/or regulatory approval. New monitoring tools will reduce costs, increase confidence in performance prediction, and promote earlier transfer of pore-space liability back to owners and provide regulators, investors and local communities with the information they need to assess site performance. The ‘fit-for-purpose’ monitoring systems will prevent unnecessary monitoring expenditures and will support permitting of new storage projects. It will support the investability in storage operations. The methodology will remove the uncertainty associated with monitoring requirements. Systems that enable validation and improved interpretation of storage data sets will allow projects to tackle problems faster, with less redundancy and higher accuracy, resolution, and frequency. The combination of advanced analytics, combined with a step change in computation power and artificial intelligence techniques, will catalyze automatic monitoring of operations, simulation, visualization, and learning while also recommending corrective actions in real time. This will reduce operational costs, shorten the time to progress, and increase confidence in large scale, safe and secure permanent storage of CO_2. Finally, newly-developed monitoring tools can be transferred across to other disciplines, including geothermal, waste-disposal, oil/gas, nuclear waste disposal industries.

Identifying and assessing anomalous signals over multiple domains outside of the storage reservoir in both terrestrial and marine environments is critically important for environmental protection, stakeholder assurance, and compliance with regulations. It also sets the basis for activating staged monitoring programs and workflows that move the monitoring through full assessment to an acceptable outcome.

With these advancements in place, methodologies for environmental assessments will be solid and dependable increasing public confidence and ensuring environmental and stakeholder protection, allowing projects to move forward without complication or doubt, and enabling gigatonne scale storage. A set of methodologies and tools that model and map the progress of projects will provide clarity to the project teams, provide a means to handle decision making covering low-probability, high-impact events and including the development of risk contingency guidelines.

The described advances will also enable higher fidelity monitoring across all domains of the system influenced by CO_2 storage operations at the gigatonne scale to ensure the monitoring program is scalable with the increasing spatial footprints of high-volume CO_2 injection and storage. This capability will significantly advance our ability to take faster, more responsive and more informed decisions when anomalous behavior is detected. This ability will in turn improve site performance and allow corrective actions (remediation and mitigation) to be undertaken in a more focused way.

Deploying permanent intelligent monitoring platforms will also allow lower-cost but more robust monitoring of the injection project during the post-closure period. Intelligent monitoring systems could be handed over to the authorities alongside the storage site thereby building confidence amongst both operators and other relevant stakeholders (e.g., communities, investors, regulators).

4.3 Storage Panel Report: Forecasting and Managing Induced Seismicity

Like any type of large-scale industrial activity, geological storage of CO_2 produces environmental and safety hazards that require careful assessment, monitoring and mitigation. Among these hazards, induced seismicity, or earthquakes attributed to human activity, has arguably produced the most visceral public reaction and vigorous scientific debate about the anticipated hazard level. As storage projects scale up to the gigatonne (Gt) level, under any scientific model, the subsurface volume affected by changes in pressure and stress will increase correspondingly, thus elevating the relative risks of induced seismicity compared with currently active projects (see the sidebar “Basic Concepts of Induced Seismicity and Monitoring”). Progress in theoretical and numerical studies is necessary to understand the complex, nonlinear systems that drive induced-seismicity processes. In addition, there is a basic disconnect between the ability to acquire large volumes of data very quickly and the slower pace at which numerical simulations and interpretations can be made. Moreover, current risk-management strategies for induced seismicity, such as traffic-light protocols (TLPs), are predominantly reactive rather than proactive in nature; whereas a range of mitigation strategies exist for sites that experience induced seismicity. Research is therefore of paramount importance to overcome critical knowledge gaps and technical barriers to improve the reliability and accuracy of hazard forecasts and the effectiveness of real-time decision making tools for management of induced-seismicity risk.

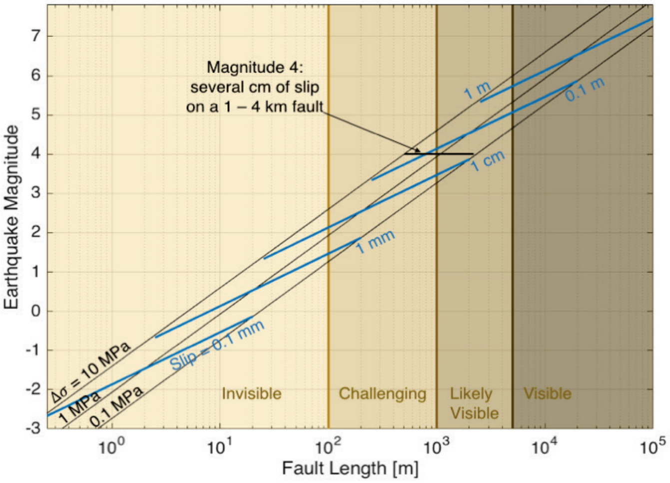
Two research areas have been formulated to address these critical knowledge gaps and technical barriers. The first is focused on improved characterization of fault and fracture systems, with the aim of highlighting geological structures that might be capable of producing damaging seismic events. These structures are typically geological faults that historically have been quiescent. The reliable identification and mapping of these features, as well as robust discrimination between them and nonhazardous faults, is a first key step in hazard assessment. Moderate-size faults pose the greatest challenge, as they may be capable of generating a damaging induced event yet may be difficult to detect without activating them. This challenge is especially acute in the case of quiescent faults that are located within crystalline basement rocks. Important opportunities exist to develop innovative, high-resolution methods to image anomalous stress fields around critical faults, which may be characterized by large-scale diagnostic signatures that are detected more easily than a moderate-size fault. Similarly, there are opportunities to improve the current understanding of fault rheological properties that control seismic slip under long-term CO_2 flooding conditions, as well as to improve links between geomechanical simulations and geophysical proxies. Progress in all of these areas will need to combine microscale laboratory studies with mesoscale field experiments and full-scale case studies.

The second research area is focused on the development of next-generation methods for seismic risk forecasting. This constitutes a scientific grand challenge because of inherent uncertainties in dealing with subsurface fields, coupled with the necessity to solve interactions among complex nonlinear systems that involve rate- and state-dependent fault rheology, complicated by strongly heterogeneous stress and fluid distributions. Independent comparison and validation among different methods is essential for progress in this PRD. Ultimately, next-generation methods must provide a robust stochastic framework to generate suites of modeled scenarios. These will enable time-efficient comparisons of a range of different mitigation measures, as well as the development of statistics-based probabilistic seismic hazard assessments derived from physics-based models. Development of risk-management schemes within this framework will support rapid, well-informed decision making that could enable injection sites to avoid triggering events that, left unmitigated, might shut down a project.

Basic Concepts of Induced Seismicity and Monitoring

“Induced seismicity” refers to earthquakes or other seismic events having a clear anthropogenic association. Large-scale underground injection of CO_2 is one example of a human activity with the potential to induce earthquakes; other examples include large-volume brine disposal, development of engineered geothermal systems, hydraulic fracturing, impoundment of surface-water reservoirs, underground mining, construction of tunnels, and detonation of underground explosions [Eaton 2018]. Various causes of human-induced earthquakes share broadly similar underlying physical mechanisms, linked to changes in the effective stresses on geological faults. Some authors use the term “triggered seismicity” to describe earthquakes that release previously stored tectonic strain energy in response to a small change in stress—in other words, events whose occurrence may have been hastened, but not entirely driven, by human activities.

The size of an earthquake is an important parameter that can be represented using various *magnitude* scales, which are logarithmic measures of the distance-corrected peak ground motion. For a given earthquake magnitude, a characteristic length scale (fault size) and slip magnitude can be estimated using empirical scaling relationships. These relationships imply that a typical magnitude 4 earthquake, for example, is associated with slip of several centimeters on a fault with a characteristic length of ~1 to 4 km. The inferred fault size provides guidance for geophysical imaging methods for site characterization, since small faults are not considered to be capable of generating a large, damaging earthquake. There is evidence that faults with certain orientations are characterized by a state of incipient failure; for faults in such a state, earthquakes can be triggered by a very small increase in fluid pressure, relative to the ambient pressure at the depth of the earthquake. Regions of the Earth’s crust containing faults in this condition are called “critically stressed” and are thought to have a high seismic sensitivity to fluid injection.



Simple empirical scaling relationships derived from earthquake observations, with expected fault visibilities using reflection seismic imaging also shown (shaded regions). Adapted from Zoback and Gorelick 2012, “Earthquake triggering and large-scale geologic storage of carbon dioxide.” *Proc. Natl. Acad. Sci.* USA 109, 10164–10168; Creative Commons User License; and *Int. J. Greenh. Gas Con.* 49, J. A. White and W. Foxall. 2016. Assessing induced seismicity risk at CO_2 storage projects: Recent progress and remaining challenges, 413–424. Copyright 2016, with permission from Elsevier.

A number of different sensors are used to monitor ground motions from induced seismicity. Each type of sensor has distinct capabilities in terms of frequency response and sensitivity. Very briefly, a seismometer is a capacitive force-balance device for measuring ground velocity and is standard instrumentation in most earthquake monitoring networks [Eaton 2018]. The sensor bandwidth depends on the application, but most modern seismometers can record ground motion with high fidelity from approximately 0.01 Hz to more than 20 Hz. Geophones are low-cost devices that passively record ground motion, typically at frequencies of 5 Hz or higher, and are standard instrumentation in controlled-source seismic methods used in the oil and gas industry. Accelerometers respond to instantaneous acceleration of the ground, using either piezoelectric ceramic transducers or a force-balance feedback principle like a seismometer. Distributed acoustic sensing is an emerging technology in which an optical fiber provides the medium for signal transmission sensing, based on coherent optical time-domain reflectometry short laser pulses.

An idealized microseismic array might consist of multiple, deep borehole arrays, with sensors that lie in close proximity to the seismogenic region while simultaneously providing large spatial coverage [White and Foxall 2016]. The expense of deep borehole deployments may not be feasible given budget constraints, and most projects to date have used a relatively small number of instruments in a shallow or deep borehole array.

Research in both of these areas will capitalize on significant advances in computational power, machine learning, and data acquisition technology, including cheaper, easier-to-deploy acquisition systems such as fiber-optic distributed acoustic sensors and autonomous nodal geophones. It will also benefit from important scientific advances and sociopolitical learning arising from induced seismicity in other domains, such as geothermal energy development and saltwater disposal (SWD).

4.3.1 Status of Forecasting and Managing Induced Seismicity Technologies

As is the case for any large-scale industrial endeavor, underground CO_2 storage involves environmental and safety hazards that require careful assessment, monitoring, and mitigation. These include the potential to induce earthquakes, which may be triggered by subsurface changes in the pore-pressure and/or effective stress conditions. As CO_2-storage projects scale up to the Gt level to achieve significant reductions in anthropogenic emissions, the affected volume of the subsurface will similarly increase, leading to an increased likelihood of stress interactions with existing faults.

The underlying physical mechanisms of seismicity induced by CO_2 injection are similar to those for other types of fluid injection, especially seismicity arising from large-scale subsurface fluid disposal. Factors that may influence the induced-seismicity rate and maximum magnitude include reservoir pressure, injection/ extraction rates, fault permeability, and initial horizontal-to-vertical stress ratio [Cappa and Rutqvist 2011; Rutqvist 2012]. In a review of induced seismicity related to energy technologies [NRC 2012], net injected volume was identified as the most important factor influencing the likelihood of induced seismicity, as it provides a proxy for changes in rock dynamics [Nicol et al. 2011]. A subsequent regional analysis of seismicity induced by wastewater disposal over a period of decades [Weingarten et al. 2015] reveals an even stronger correlation with injection rate at individual wells.

In aggregate, Gt-scale SWD from oil and gas development in the central United States has led to a major recent surge in induced earthquakes, including events as large as magnitude (M) 5.8. This has contributed to heightened public concern and new regulatory challenges [GWPC 2015]. In Oklahoma, the scale of the seismicity response has confirmed that, at least in some areas, stress changes of only a few percent are sufficient to trigger earthquakes (see the sidebar "Lessons from Oklahoma." The implied state of incipient failure of the crust has significant implications for seismicity risk at CO_2 sites, prompting vigorous academic debate. Some researchers have argued that induced seismicity risks due to underground CO_2 storage are unacceptably large [Zoback and Gorelick 2012], whereas others contend that risks can be managed [Vilarrasa and Carrera 2015].

One underlying reason for the diversity of scientific viewpoints may be the complex, site-specific, and evolving nature of the seismicity response at CO_2 storage operations. Representative examples are listed in Table 4.1, highlighting experiences from CO_2 sequestration projects for which seismicity data are available. At the Weyburn CO_2 Enhanced Oil Recovery (EOR) Project in Canada, the first project to deploy instrumentation for monitoring seismicity, annual net storage of 2.7 megatonnes per year (Mtpa) has been achieved. Yet only ~100 microseismic[2] events in the M3 to M1 range were recorded over a 7 year period. In contrast, more than 10,000 events from M2 to M1 were detected during 22 months of monitoring during CO_2 injection for the Decatur Project in Illinois. Data collected and analyzed by two independent groups reveal linear trends of microseismicity, consistent with activation of small faults within the basement rock below the injection level. Seismicity at the In Salah CO_2 storage project in Algeria is characterized by slightly larger magnitudes than at Decatur. The seismicity at In Salah was accompanied by surface deformation that was detected by satellite using interferometric synthetic aperture radar (InSAR). The surface deformation occurred in response to high-pressure injection into a sandstone layer intersected by subvertical faults [Rutqvist 2012]. In an EOR project at the Cogdell Field in Texas, earthquakes up to M4.4 were observed during high-rate gas injection; in contrast, injection at the nearby Kelly-Synder field, within the same reservoir unit and along the same structural trend as

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[2] There is no general agreement on the magnitude range implied by the term "microseismic" [Eaton 2017]. Here, it is applied to events with $M < 2$, which are generally not felt at the surface.

Cogdell, generated no detectable seismicity [White and Foxall 2016]. Despite the limited number of available examples, it is clear that induced seismicity behavior is highly site- and operation-specific.

Table 4.1. Summary of seismicity observations at CO_2 injection sites. | Modified from White and Foxall 2016

Site	Type	Operation	Monitoring	Observations
Aneth (USA)	CO_2 EOR		Borehole microseismic	Magnitudes: M1.2 to M0.8 Frequency: 3800 events over 1 yea. Two fault-like clusters
Cogdell (USA)	CO_2 EOR		Regional network	One M4.4 event and 18 M3+ events over a 6 year period. No major seismicity at nearby, similar operations
Weyburn (Canada)	CO_2 EOR	2000 ~ 3 Mtpa	Borehole microseismic	Magnitudes: M3 to M1. Frequency: 100 events over 7 years Diffuse locations
Decatur (USA)	CO_2 disposal	2011–2014 1 Mtpa	Borehole microseismic and surface array	Magnitudes: M2 to M1 Frequency: 10,123 events over 1.8 years Multiple fault-like clusters
In Salah (Algeria)	CO_2 disposal	2004 ~ 1 Mtpa	Shallow borehole microseismic	Magnitudes: M to M1.7 Frequency: 10,000 events over 1 year Indications of fracture stimulation
QUEST (Canada)	CO_2 disposal	2015 ~ 1 Mtpa	Borehole microseismic array	<100 microseismic events from a localized source region in the basement

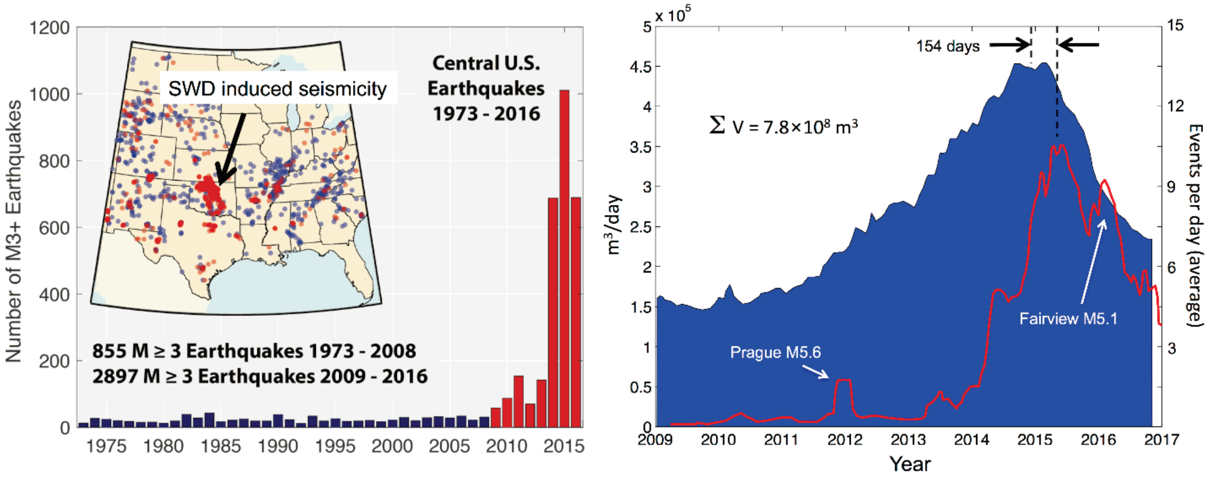
In contrast to most wastewater disposal projects, CO_2 storage projects routinely make use of 3D (and often 4D) seismic methods for site characterization [White and Foxall 2016]. In principle, this approach enables the detection and mapping of nearby geological faults that are capable of producing large earthquakes. There are, however, inherent limits in the ability to identify faults via seismic characterization. Problematic cases include unfavorable fault geometries, such as subhorizontal thrust faults or vertical strike-slip faults in horizontally stratified rocks, and an absence of reflection terminations for faults located within crystalline basement rock. Moreover, moderate-size faults that are sufficiently large to produce seismicity of concern may fall below detection limits for 3D seismic methods. As illustrated by the Decatur project, microseismic events observed during injection can also be used to delineate faults. Indeed, there is growing recognition of the value of microseismicity for understanding the geomechanical response of a reservoir (see the sidebar “Microseismicity: Friend or Foe?”)

Lessons from Oklahoma

What are the consequences of injecting ~1 Gt of fluid into a seismically sensitive zone? Since 2009, an unprecedented increase in the rate of small-to-moderate earthquakes in the US midcontinent has been triggered by high-volume SWD into a multitude of wells that inject fluids associated with oil and natural gas production [Weingarten et al. 2015]. For a number of years, Oklahoma, the most heavily impacted state, held the dubious distinction of being the most seismically active state per unit of area in the lower 48 states [Keranen et al. 2014]. Seismicity rates peaked in 2015, partly in response to regulatory measures to reduce injection volumes into the most problematic injection zone, the Arbuckle Group [Langenbruch and Zoback 2016].

The overall scale of the problem is illustrated in the images below. The diagram at left shows the annual rate of earthquakes from 1973 through 2016 above the threshold of completeness (M ≥ 3), along with event locations (inset). Post-2008 earthquakes are plotted in red, highlighting the spatial and temporal extent of the recent surge in seismicity. The graph at right compares the injection rate into the Arbuckle Group with a 90 day running average of seismicity rate. Even after smoothing, discernible secondary peaks are clearly associated with aftershock sequences from the Prague and Fairview earthquakes. An approximately 5 month lag between the injection maximum and peak seismicity rate most likely reflects the time required for pressure diffusion within the subsurface [Langenbruch and Zoback 2016].

This dramatic case of injection-induced seismicity provides several key lessons for geological carbon storage, especially in view of the similarity in scale to envisioned Gt-scale CO_2 storage initiatives. While the increase in seismicity has drawn worldwide attention, the ensuing decrease is broadly indicative of the time-dependent large-scale response of the complex system and offers encouragement that mitigation measures can be effective even on this large scale. Moreover, intense research by many groups has greatly improved scientific understanding of the phenomenon, including timely improvements for a site characterization framework to avoid repetition of this scenario.

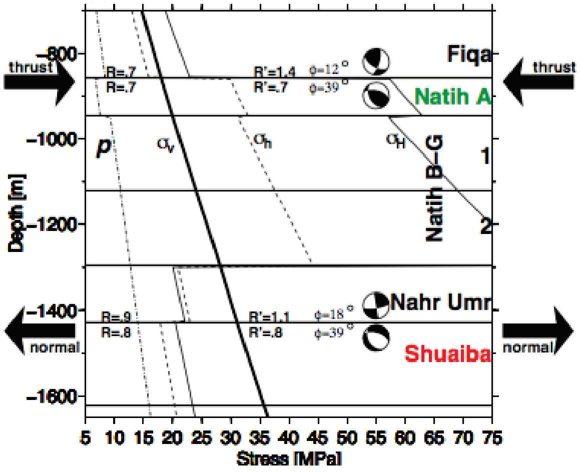


Left: Graph of M≥3 earthquakes per year within the US midcontinent (region shown in the inset map). Increased rates of seismicity after 2008 are highlighted in red. | Images courtesy of US Geological Survey.

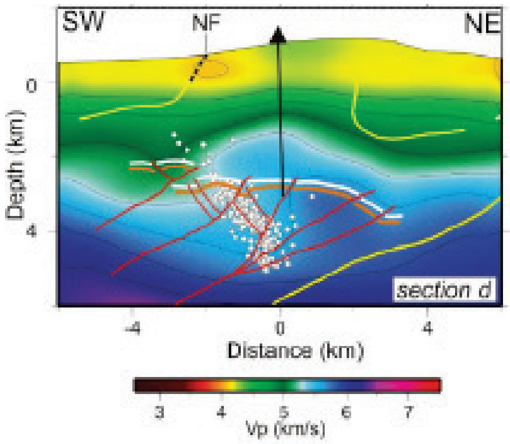
Right: Comparison of daily injection rate into the Arbuckle Group in Oklahoma (blue area) with 90-day running average of number of earthquakes (M≥2.5) per day. The total injected volume over this time is ~0.8 Gt (1 m^3 water ~ 1 tonne). A lag of 154 days is evident between the two times indicated, which mark the approximate peak times for injection and seismicity rate, respectively. | Data from Boak 2017. Patterns of Induced Seismicity in Central and Northwest Oklahoma. Accessed September 29, 2017.

Microseismicity: Friend or Foe?

Microseismicity during CO_2 injection is sometimes considered unfavorable. In fact, microseismic observations are a valuable geophysical tool for understanding the reservoir response to CO_2 injection. For example, microseismic event locations may be used to map the CO_2 plume geometry or to image small faults that are not visible using other geophysical methods. Further, microseismic source mechanisms can be inverted to reveal spatial variations in stress conditions across a reservoir (left panel). Microseismic events also represent seismic sources that can be used to image temporal changes in seismic velocities and anisotropy (right panel). These observations can be used to map fluid movement and permeability changes within the reservoir and recognize fracturing of the cap rock. Therefore, microseismicity, so long as it does not increase in magnitude so that it poses a seismic hazard, is a friend, not a foe, to the CCUS industry.



Variations in stress conditions with depth across different formations in a producing oil reservoir, inverted from observations of microseismicity. | From A. S. Al-Anboori. 2005. "Anisotropy, Focal Mechanisms, and State of Stress in an Oilfield: Passive Seismic Monitoring in Oman." PhD thesis, University of Leeds



Ratio of P- to S-wave velocities (V_P/V_S) at the Val d'Agri oilfield, mapped using seismic tomographic methods. V_P/V_S can be an important parameter for identifying changes in fluid properties. | From Improta et al. 2017

Geomechanical modeling studies for simulating fault reactivation and other geomechanical processes during CO_2 injection are reviewed by Rutqvist [2012]. Models can be developed using fault architecture and rock mechanics data acquired during site characterization. Some simulation methods use a coupled approach that combines fluid flow with geomechanical deformation. Many of these analyses indicate that fault reactivation from CO_2 injection is closely linked to the injection pressure, but there is a high level of uncertainty in terms of the ambient stress field as well as the assumed frictional properties of faults.

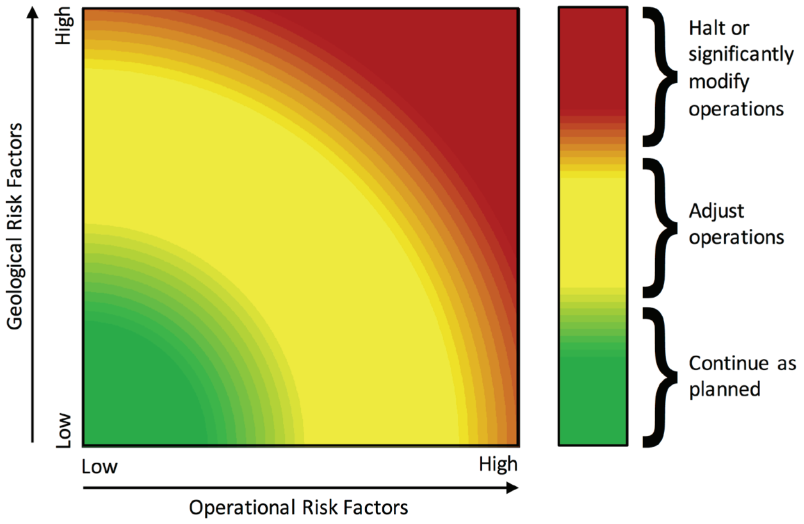
The term "hazard" describes the probability of occurrence of a potentially damaging event. Potential hazards from induced seismicity range from public nuisance to property damage, injuries, and loss of life from ground shaking, or contamination of groundwater due to loss of seal integrity. Methods to quantify hazard from earthquakes are based on the probability of exceedance of a particular level of ground shaking within an application-specific time interval. Probabilistic hazard forecasting methods are typically formulated using a catalog of past earthquakes, whereas deterministic methods are based on numerical simulations of scenario events on a known fault system. Both methods can be combined with empirical ground-motion prediction models that capture ground-shaking intensity as a function of distance. At present, statistical models provide the most robust approach for forecasting seismicity, but the use of physics-based approaches for scenario events may be key in the future [IEA 2013].

The concept of risk is generally represented as the product of hazard and other factors such as exposure, fragility, and consequence (known collectively as vulnerability [Bommer et al. 2015]. Risk can be reduced through a systematic, structured risk-management program similar to those developed for enhanced geothermal systems [IEA 2013], which include the use of TLPs (see the sidebar "Traffic Light Protocols"). Because of the dynamic complexity inherent to earthquake systems, there will always be an irreducible chance of inducing larger earthquakes. Hence, it is pragmatic to select sites with low vulnerability and develop engineering safeguards so that consequences are low, even if induced seismicity occurs [White and Foxall 2016].

Traffic-Light-Protocols: Can They be Proactive?

A TLP is a reactive-control scheme with multiple discrete response thresholds, in which each threshold invokes action designed to mitigate a specific risk. In the case of induced seismicity, TLPs have been implemented using fit-for-purpose seismograph arrays with real-time processing, together with region-specific operational protocols for "green," "amber," and "red" light conditions (e.g., Eaton [2018]). These systems are employed by operators and regulatory agencies as pragmatic decision-making tools, based on the principle that potentially damaging ground motion can be avoided by timely modification of injection operations. A number of deficiencies in some current TLP systems have been noted [Kao et al. 2016]), including issues arising from uncertainty in magnitude calculations, a need to employ additional real-time hazard measures such as peak-ground acceleration, and a desire for a more risk-based approach tied to specific consequences of induced seismicity.

The development of a proactive TLP for induced seismicity could entail the early detection of the onset of seismicity patterns that are considered to be indicative of nucleation of a large event [Eaton 2018]. Such patterns may include a change in the slope of the magnitude-recurrence relationship (*b*-value), an increase in seismicity rate above a specified threshold, or the emergence of event lineations in an alignment that is favorably oriented for fault activation. In addition, the use of a hazard-matrix approach, as illustrated in the diagram below, facilitates the incorporation of geological and operational risk factors.



Hazard-matrix approach for TLPs. | Image courtesy of David Eaton, University of Calgary

4.3.2 Scientific Challenges

For gigatonne-scale carbon sequestration projects, several key research challenges must be addressed to develop and deploy effective technology for forecasting and managing induced-seismicity risk. These research challenges involve a number of critical knowledge gaps:

- Fully characterizing the induced seismicity risk of a site/region before the start of injection
- Optimally designing monitoring systems
- Developing proactive mitigation strategies to inform real-time decisions during operations
- Understanding the impact of cumulative effects, adjacent operations, and long-term consequences at time scales that extend long after project completion

These knowledge gaps are outlined in the following pages. The research required to address these gaps extends well beyond what can be achieved through incremental improvements in current technologies.

Fully characterizing the induced seismicity risk of a site/region before the start of injection

Risk assessment is the first step in risk management. For induced seismicity, this step involves identification and mapping of subsurface geological faults as a prelude to quantitative risk analysis [Walsh and Zoback 2016]. Induced earthquakes are thought to occur on well-oriented faults that are critically stressed (i.e., prone to failure in response to a small perturbation in stress state). Yet in continental interior regions, faults that are most readily identified and mapped using classical geophysical imaging methods (e.g., offset reflections in 3D seismic methods) may not be activated even if they are well oriented for activation in the present-day stress field. Instead, problematic faults are often cryptic, on the basis of well-established methods of site characterization. These cryptic faults, or geohazards, tend to become apparent only after the fact, when they are illuminated during injection by patterns of seismicity. Current geophysical methods for identifying and mapping potentially seismogenic, but historically quiescent, faults in continental interiors can be considered to be at a low level of technology readiness, as these methods suffer from unacceptably high rates of both missed events and false detections. Robust techniques to map critically stressed faults in 3D and distinguish them from faults that are not prone to earthquakes are thus a priority.

More research on inactive faults is also needed to improve our understanding of their rheology, state of stress, and permeability evolution. Possible modes of fault reactivation include aseismic slip or dynamic rupture, with or without substantial permeability change [White and Foxall 2016]. Although the basic physical framework for effective stress is well established, our understanding of several critically important details remains incomplete. Examples of knowledge gaps include the possible role of fault cohesion in historically quiescent faults, conditions under which fault permeability increases or decreases in response to seismic rupture, improved understanding of the nucleation and arrest of dynamic rupture on a pressurized fault, and, more generally, why some faults creep while others produce dynamic rupture. As noted by Verdon et al. [2013], as part of the site-characterization process there is also a need to develop site-specific geomechanical models. There is a further need to develop stochastic geomechanical modeling approaches that incorporate realistic geological uncertainty. At present, we lack integrated models, and those that exist are not unique or do not meet performance expectations. Given current state-of-the art reservoir modeling codes, rheological and permeability characteristics and evolution are not sufficiently well understood, including static and dynamic stress changes and their effects on permeability.

Optimally designing monitoring systems

For a Gt-scale CO_2 project, design criteria for induced-seismicity monitoring systems will likely include the following:

- Real-time data streaming capabilities with performance standards for acceptable network and station down-time
- A site-specific uniform magnitude-detection threshold over the monitoring region to ensure catalog completeness, along with sufficient coverage of the seismogenic zone to ensure well-constrained focal mechanisms

- Seamless integration of various types of monitoring data, potentially including different types of ground-motion sensors (seismometers, geophones, accelerometers, fiber optic systems), other types of deformation sensing devices (precise geodetic systems, InSAR, tiltmeter) and other types of data (temperature, pressure)
- Conformance with triggering parameters for site-specific TLPs
- Open data access for full public transparency and to support independent scientific research

There are inevitable cost-benefit trade-offs in the design of any network, as ideal network designs such as multiple deep borehole sensor arrays may be cost-prohibitive for some projects. Nevertheless, real-time monitoring (24/7) is essential to inform timely decision processes during any episode of induced seismic activity, in accordance with mitigation processes discussed below. The determination of a magnitude-detection threshold will depend upon baseline seismicity observations, local regulatory requirements, and forecasting derived from site characterization. The region of coverage for the monitoring network must extend outside of the region of injection wells to provide adequate coverage of neighboring seismogenic regions. Flexible data integration of multi-sensor networks is likely to be an increasingly important consideration in the future, as new technologies are developed. For example, the use of fiber-optic distributed acoustic sensing may become standard as part of future "smart well" designs. In a pervasively connected and increasingly demanding public sphere, full transparency and open data access will be essential for gaining public trust in large-scale projects.

Developing proactive mitigation strategies to inform real-time decisions during operations

Current risk-management strategies for induced seismicity, such as TLPs, are predominantly reactive in nature. For example, earthquake processes are stochastic, and the largest events may occur early in an induced earthquake sequence with little to no warning. In such a scenario, TLPs and injection-rate control techniques may be rendered ineffective. Hence, there is a need for better, more robust, short- to medium-term[3] probabilistic forecasts of induced seismicity in real time. Numerical weather prediction (NWP) is an appropriate analog; like the induced seismicity problem, NWP involves probabilistic forecast models derived from solutions to complex dynamical systems with both grid-resolvable components (pressure-gradient force, advective transport, Coriolis force, large-scale buoyancy) and sub-grid components (cloud microphysics, boundary layers, turbulence, topographic and vegetation effects).

At present, there is lack of certainty among stakeholders and regulators about what a good seismicity management plan looks like. Before an induced event, possible risk-reduction options may include

- Avoidance of hazardous faults
- Seismic retrofits for buildings
- Injection program design using very remote locations, including offshore

In confronting a significant induced event, mitigation options may include

- termination or reduction of injection rates
- dispersion of injection into other wells or injection into a different formation
- management of pressure by brine extraction
- attempting to induce fault creep instead of dynamic rupture

As an example of a strategy for pressure management by brine extraction, a push-pull method called "active CO_2 reservoir management" has been proposed by Buscheck et al. [2011]. This method combines

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[3] Timescales that define "short" and "medium" term will necessarily be operationally dependent - i.e., determined by measures that are practical to implement in the field immediately (short term), versus those need to be managed on a longer timescale within the CO_2 capture and transportation supply chain (medium term).

CO_2 injection with brine extraction and residual-brine reinjection. It is in contrast to conventional passive CO_2 reservoir management. The fourth option, inducing fault creep, remains speculative at the current level of knowledge.

At the crux of the present technology bottleneck is a basic disconnect between the ability to acquire large volumes of data very quickly versus the current inability to compute simulations and interpretations to keep pace. At present, researchers lack integrated models that meet performance expectations, and project operators have limited time to understand and react to these evolving hazards. Better data analysis and modeling techniques, soundly based on the physics of induced seismicity, are therefore required. Technical barriers to accelerating and upscaling simulations stem from the fine-resolution/mesh requirements, combined with the large regional extent of the monitoring systems. The situation is compounded because felt events resulting from injection activities have the potential to alarm nearby communities; so the lower-bound magnitude of concern for induced seismicity (about M1.5 – M2) is lower than the level that is typically the focus of natural seismic risk assessment (usually ~M4.5).

Understanding the impact of cumulative effects

The final knowledge gap considered emphasizes the primary importance of accommodating, within numerical simulation models and monitoring capabilities, the full spatial scale (1000s of km^2) and temporal scale (decades or centuries) of CO_2 storage systems. The former element focuses on the probable need to consider the cumulative effects of multiple CO_2 plumes from distributed injection wells within a single storage project. The latter element focuses on the need to forecast the long-term, likely intergenerational, induced seismicity consequences of storage systems, including those that may occur long after project completion.

Another important consideration is the potential for complex interaction with other dynamic systems of fluid injection and withdrawal. Considering future growth in energy needs, other projects located within the footprint of a Gt CO_2 storage system could include conventional oil and gas and EOR projects and/or geothermal programs. It is therefore important to evaluate the system behavior beyond an isolated reservoir model, both at a regional scale and over a long time scale.

The requirements to address these knowledge gaps are outlined in two PRDs for forecasting and managing induced seismicity:

1. Enhanced Characterization of Fault and Fracture Systems
2. Next-generation Seismic Risk Forecasting

Both PRDs will require significant progress in the understanding of earthquake science, reservoir geomechanics, seismology, and risk engineering, making use of new technologies such as fiber optics and real-time acquisition of big data from field observations. Progress in theoretical and numerical studies will be necessary to understand the complex, nonlinear system of the induced seismicity processes, taking into account inherent strong heterogeneities and significant uncertainties. Fault-zone rheology will be investigated through mesoscale experiments that will span microscopic and macroscopic scales of understanding. Management of induced seismicity will need to be accompanied by research efforts to improve the basic understanding of the highlighted knowledge gaps, including limitations of reactive management methods.

4.3.3 Why Now?

Public awareness of induced seismicity has increased substantially in recent years, to the point that concerns around seismic hazard could pose an existential threat to industrial projects in some areas. These concerns have produced an increase in the intensity of research being performed in this field, which has improved our basic understanding but also highlighted important knowledge gaps. In light of the growing number of subsurface injection sites around the world, associated with a range of industries, research into induced seismicity is timely.

Research in this field is poised to benefit from recent advances in both acquisition technology and computational power. Cheaper, easier-to-deploy acquisition systems—such as fiber-optic distributed acoustic sensors and autonomous nodal geophones—mean that large, dense arrays can be installed in both surface and downhole configurations, thus providing opportunities for significant improvements in data quality. Increases in computational power will enable processing of large data sets in real time to facilitate stochastic geomechanical simulations that are necessary to perform physics-based probabilistic seismic hazard assessment.

As the number of well-monitored case studies of induced seismicity grows, scientists are beginning to develop a sufficient sample of data sets from which general conclusions can be drawn. With increased data set availability, modeling strategies can be evaluated across a range of settings. Dedicated field experiments are also under development, which offer the promise for opportunities to further improve understanding of fault behavior in response to injection.

4.3.4 Conclusion

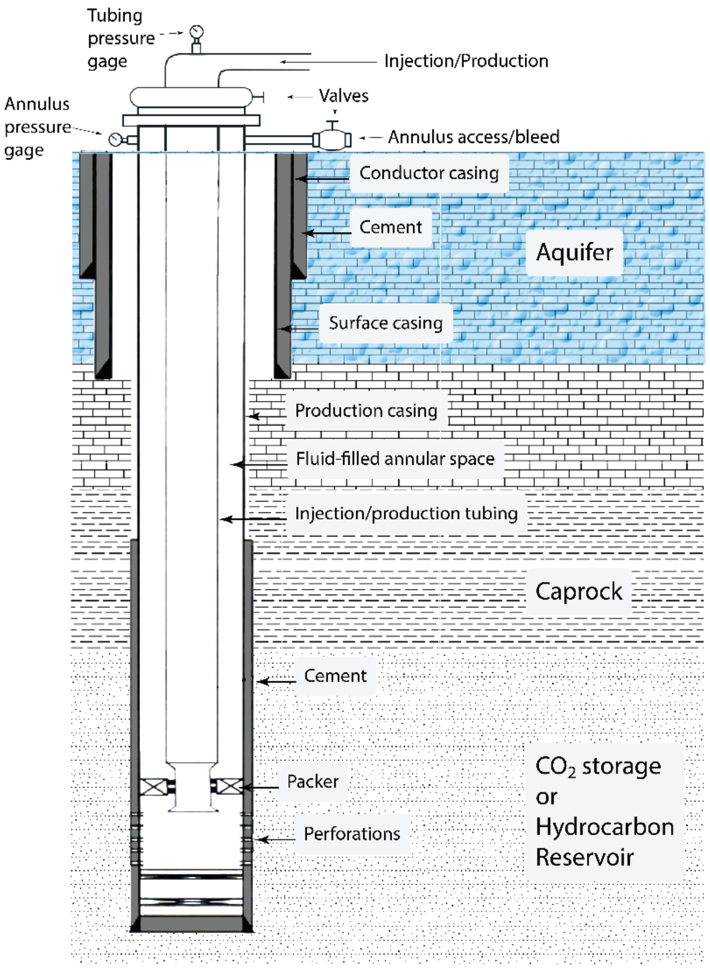
Research challenges for induced seismicity require multidisciplinary approaches based on observation, theory/numerical studies, and experimental experiences and on fundamental scientific understanding, monitoring and analysis technology, risk management, and public relations. Beyond the state of the current knowledge, based on the scale of a single reservoir, future projects require assessment on a regional scale. During such upscaling, fundamental questions will be encountered, including regional stress fields and inactive fault behavior. It is expected that the progress in each component for better managing induced seismicity will provide assurance of CO_2 storage integrity through the mitigation of risks related to induced seismicity.

4.4 Storage Panel Report: Well Integrity

Wells are the primary means of accessing, characterizing, and monitoring the subsurface. Large-scale, geological storage of CO_2 will require extensive deployment of purpose-built CO_2 injection and monitoring wells. In addition, CO_2 storage sites will inevitably contain previously drilled wells for oil and gas, water extraction/disposal, and other uses. All of these wells represent a potential leakage pathway for migration of CO_2 and brine from the storage reservoir. Well integrity can be defined as the "application of technical, operational and organizational solutions to reduce the risk of uncontrolled release of formations fluids and well fluids throughout the life cycle of the well" [NORSOK 2013]. By this definition, successful CO_2 storage operations must ensure well integrity as part of a comprehensive strategy to permanently sequester anthropogenic CO_2. Risk assessment studies consistently identify poor well integrity (i.e., leakage from wells) as a dominant risk factor for CO_2 storage [Pawar et al. 2015; FutureGen 2007; Metz et al. 2005]. Some potential storage sites (particularly depleted oil and gas fields) may have tens to thousands of wells. For example, the Weyburn-Midale CO_2 storage project involved a study of 1,424 wells [Duguid et al. 2017], and the US Environmental Protection Agency estimates that there are more than 1.2 million active wells in the United States as of 2014 [EPA 2015].

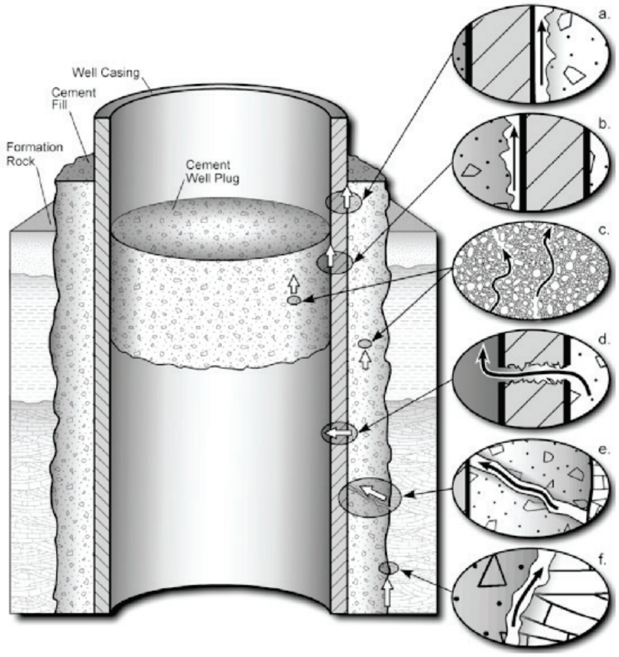
Considerations of well integrity can be divided into three distinct phases: (1) during drilling and completion, (2) during operational aspects of production or injection, and (3) after abandonment. This report focuses on the post-drilling and completion phases when the problem lies in evaluating the integrity of barriers consisting of mechanical devices, cement, and steel placed downhole to isolate subsurface fluids (see the sidebar "Elements of Wellbore Systems and Leakage Paths"). A well integrity failure may be a readily observed blowout (an acute release; e.g., the Aliso canyon methane release [Conley et al. 2016] or the Sheep Mountain CO_2 release [Lynch et al. 1985]). Or it may involve chronic release—a difficult-to-observe, slow migration of gas or liquid that ultimately causes some form of environmental damage or threat to human safety (e.g., Lloydminister, Canada [Erno and Schmitz 1996] or hazardous migration of methane in Pennsylvania [Considine et al. 2012]). Well integrity issues can be further distinguished as occurring in active wells or in plugged and abandoned wells and in onshore versus offshore environments. Characterization and remediation operations are relatively more easily accomplished in an active well where instrumentation can be readily introduced downhole.

In an ideal world, a technology would exist that would enable drilling and completion to create 100% perfectly sealed wells that are impervious to subsequent stress and damage. The reality is that isolation of fluids has to occur far below the surface, at depths of 1–3 kilometers, in small-diameter holes (10–15 cm), presenting significant scientific and technological challenges. Improvements are needed, starting with the well construction process and extending beyond abandonment, to significantly reduce or eliminate the risk that leaking fluids will cause damage to the biosphere or subsurface resources (e.g., groundwater and oil and gas reserves).



Elements of Wellbore Systems and Leakage Paths

The panel at left illustrates an active injection or producing well that consists of a series of nested steel casings that are cemented into the borehole. The central tubing either injects fluid into or produces it from the reservoir and is isolated from the rest of the well by a packer. Perforations through the casing allow fluid to exit or enter the well. In most jurisdictions, the surface casing is used to protect groundwater resources and must be cemented to the surface. Multiple barriers are used to protect against leakage, including cement, production casing, packer, and tubing. Leakage within the well would be detected as elevated annulus pressure; leakage external to the well would impact the aquifer. | Image by William Carey. Used by permission



The lower panel shows a close-up of an abandoned well with a cement plug placed inside the production casing. Several possible leakage mechanisms are illustrated:

- flow along the casing–cement interface (microannulus)
- flow between the cement plug and casing
- flow through damaged, permeable cement
- flow through corrosion-induced hole in casing
- flow through fractures in cement
- flow between cement and caprock
- flow through damaged caprock (not illustrated)

Lower image reprinted from *Proceedings of the 7th International Conference on Greenhouse Gas Control Technologies,* **1**, 5 September , M. Celia et al. Quantitative estimation of CO_2 leakage from geological storage: Analytical models, numerical models, and data needs, 663–671. Copyright 2005, with permission from Elsevier

Research needs include an improved understanding of thermal-chemical-mechanical stresses that exist in the downhole environment. This would lead to new construction practices with new materials that are fit-to-purpose, self-repairing, and capable of withstanding long-term stress. Improved monitoring methods are needed that conclusively demonstrate the presence or lack of well integrity, that detect and quantify the locations and fluxes of migrating fluids, that can be operated remotely, and that can characterize abandoned wells and those in both onshore and offshore environments. Risks associated with both new and old wells must be quantified, which will require analysis of historical data and the development of predictive models of well performance. Finally, despite best efforts, well failures will require effective remediation in all environments, including abandoned wells.

The Well Integrity panel developed two research directions addressing these needs. The first PRD looks back in time at the challenges of ensuring well integrity of existing and abandoned wells. The second looks forward to the development of new technology and the problem of ensuring the long-term integrity of built-for-purpose CO_2 storage and monitoring wells.

4.4.1 Status of Wellbore Integrity Technologies

Over the nearly 200 year history of oil and gas development, the concept of well integrity has gradually developed and is now implemented through the concept of installing multiple barriers (e.g., casing, cement, packers) so that failure of any single element does not lead to escape of fluids to the external environment [King and King 2013]. Nonetheless, failure of one or more barriers has been observed in the form of gas pressure accumulating within the annulus of the well [Watson and Bachu 2009; Wojtanowicz et al. 2001] and gas migration external to the well [Bachu 2017; Erno and Schmitz 1996] and documented in regulatory agency records [Davies et al. 2014; Lustgarten 2012]. In terms of risk, the critical assessment is of environmental damage linked to well integrity, for which relatively few data are available. However, Kell [2011] and Osborn et al. [2011] appear to show that the rate of environmental damage is significantly lower than reports of barrier failure [Pawar et al. 2015].

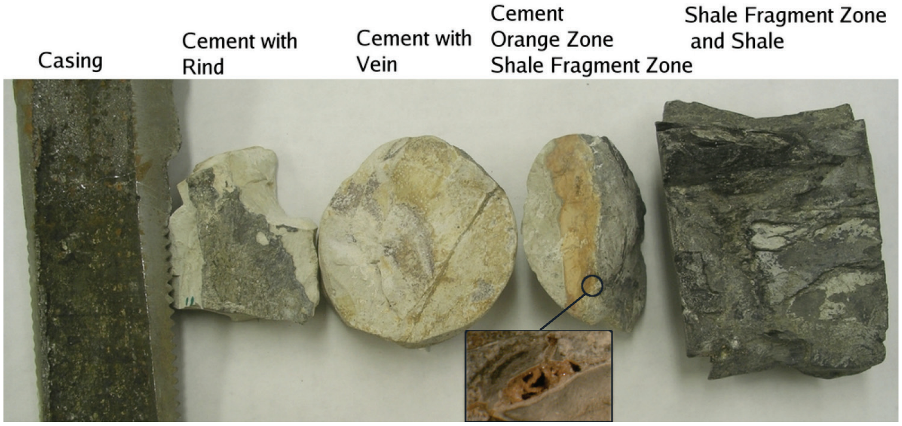


Figure 4.8. Recovery of casing, cement and caprock in sidetrack-coring operation showing migration of CO_2 along the cement-shale interface ("orange zone"). The inset shows carbonate precipitation and self-sealing of the interface. | Modified from *8th International Conference on Greenhouse Gas Control Technologies*, J. W. Carey et al. Analysis and performance of oil well cement with 30 years of CO_2 exposure from the SACROC Unit, West Texas, USA, 75–85, Copyright 2007, with permission from Elsevier

Well integrity failure can originate from poor construction or from post-completion thermal, chemical, or mechanical stresses [Carey 2013]. In principle, inadequate construction can be identified through the use of downhole well-inspection methods. The impact of chemical stress on wells in CO_2 sequestration has been reviewed by a number of authors, including Carey [2013], Carroll et al. [2016], Choi et al. [2013], Randhol and Cerasi [2009], and Zhang and Bachu [2011]. Field studies of CO_2-enhanced oil recovery sites and natural CO_2 reservoirs demonstrate that wellbore systems can survive CO_2 environments (Figure 4.8) [Crow et al. 2010].

A number of laboratory experiments have characterized CO_2-brine leakage processes through damaged cement, [Huerta et al. 2016], simulated casing–cement interfaces, [Carey et al. 2010; Wolterbeek et al.

2016] and cement–formation interfaces [Kjøller et al. 2016; Newell and Carey 2013; Walsh et al. 2013]. Very little is understood about leakage that might occur through drilling-damaged caprock. In general, laboratory studies of fractures or defects in Portland cement have shown that it is remarkably resilient in the face of acid attack by CO_2-bearing fluids and is capable of self-sealing via a combination of carbonate precipitation and mechanical yielding of amorphous silica residue (Figure 4.8) [Walsh et al. 2013; Wolterbeek et al. 2016]. A theory to predict self-sealing behavior has been developed by Brunet et al. [2016] as illustrated in Figure 4.9, but significant work is needed to generalize this result for application to long-term assessment of leakage risk. Issues related to corrosion are little understood except, perhaps, in the context of simple exposure of metal to CO_2-bearing fluids [Choi et al. 2013]. For example, little is known of corrosion rates and impacts when aggressive (e.g., CO_2- or H_2S-bearing) fluids attack the composite steel-cement system.

The literature on mechanical stress has emphasized borehole stability (i.e., open boreholes without casing and cement). Frash and Carey [in press] discuss the more limited numerical analyses of stress in completed wells. The mechanical integrity of wells depends crucially on understanding the initial stress state of the cement-casing-formation system, for which few data exist [Bois et al. 2011; Frash and Carey in press]. Most models proceed with an assumed initial stress state and characterize mechanical damage in terms of delamination of the interface or fractures in the cement [e.g., Feng et al. 2017; Lecampion et al. 2013; Nygaard et al. 2014]. Thus far, most models have not been tied to the laboratory (but see [Lecampion et al. 2013]) or to field observations, and the understanding of mechanical stress on wells is inadequate.

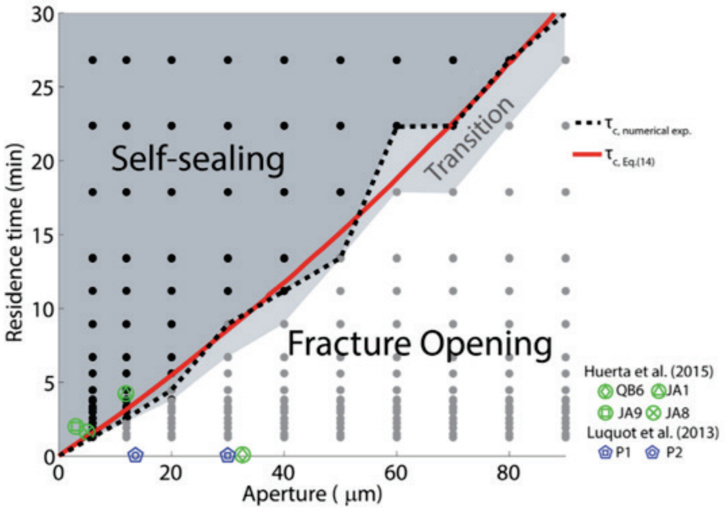


Figure 4.9. Numerical simulation of self-sealing and cement fracture opening as a function of fracture aperture and fluid residence time. | From Brunet et al. Fracture opening or self-sealing: Critical residence time as a unifying parameter for cement–CO_2–brine interactions. *Int. J. Greenh. Gas Con.* **47**, 25–37. Copyright 2016, with permission from Elsevier

Flow and reaction cannot proceed without a path created by either a defect in construction or stress-induced mechanical failure. Once that flaw exists, CO_2-bearing fluids can migrate from the storage reservoir; the migration leads either to increasingly open fluid pathways (through dissolution of cement and caprock or by corrosion of steel) or to a self-limiting condition in which mineral precipitation (e.g., calcium carbonate) or stress-induced deformation closes the gap [Carey 2013]. Such coupled processes have been little studied, and understanding them is necessary for the development of long-term predictive models of well performance.

Many issues in well integrity could be addressed through effective monitoring technology capable of detecting defects in construction, stress-induced fractures and interfaces, and leaking fluids. Current technology for characterizing the adequacy of cementing relies on sonic and ultrasonic acoustic methods [API 2008; Duguid et al. 2017]. These so-called "wireline" tools are lowered into the well and interrogate the casing-cement-formation system. They provide measures of the presence of cement, the density of cement, cement contamination by gas or liquid, and bonding with the casing (and, to a lesser extent, the formation). These techniques appear capable of demonstrating when regions of wells have clear problems; in general, they do not "prove" integrity or the lack of leakage paths. The issue is further complicated by the fact that poor cementing in one region of a well does not preclude another (possibly quite small) length of the well from providing an effective seal. Obviously, logging provides an assessment only when it is carried out; and because of the cost, it is unlikely to be repeated unless other observations suggest a problem or regulations require it. Some new wells are being instrumented with permanent sensors (e.g., optical fiber), but the challenge is to do so in a way that does not jeopardize well integrity nor interfere with well operations such as perforations. Data transfer technology and the longevity of sensors/cables are also challenges.

There are other similarly invasive methods of assessing well integrity, such as pressurizing the internal annulus of the well to verify the internal integrity of the well and several tools for assessing external integrity [Nielsen and Aller 1984; Thornhill and Benefield 1992]. The latter include the use of acoustic noise logs, temperature logs, and radioactive tracer logs that specifically target the movement of fluids behind casings.

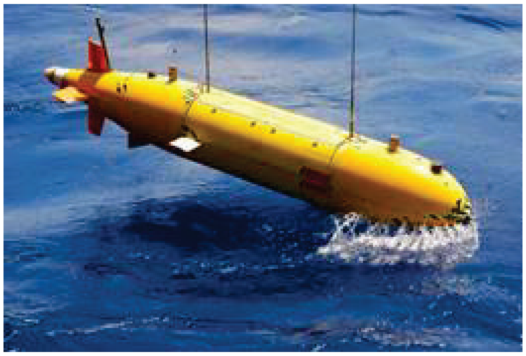


Figure 4.10. (a) Novel remote sensing under water with autonomous underwater vehicle and (b) airborne electromagnetic sounding using a torus helium balloon. | (a) image from CTEMM-CCS website (http://www.stemm-ccs.eu/work-packages). Used by permission of Doug Connelly, National Oceanography Centre, UK.

These monitoring techniques do not address the most problematic of wells, those that are plugged and abandoned. Regulations require that when wells are retired, cement and mechanical plugs be placed inside at critical depths necessary to protect groundwater, and the steel tubing be cut off below the surface and capped [King and Valencia 2014]. This practice precludes the use of the downhole (wireline) techniques described previously. Therefore, plugged and abandoned wells are assumed to be high risk. At present, methods for remotely monitoring such wells are based on detecting emissions or other environmental signals, including soil gas and atmospheric detection (Erno and Schmitz 1996; Kang et al. 2016; Townsend-Small et al. 2016] and electrical resistivity/conductivity measurement [IEAGHG 2012; Kell 2011]. New concepts include autonomous vehicles (Figure 4.10). In some cases, even the locations of abandoned wells are unknown, and various techniques such as magnetic surveys have been used to find them (Figure 4.11) [Hammack et al. 2006].

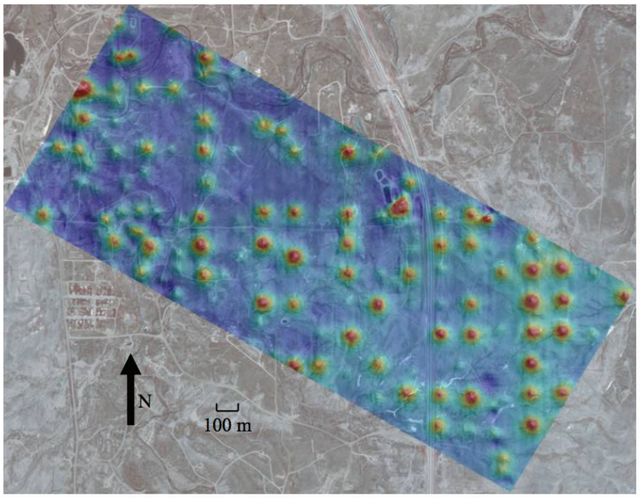


Figure 4.11. Helicopter-based magnetic field survey at a CO_2-enhanced oil recovery field showing locations of wells in a 1 square mile region. A simultaneous study of methane emissions located leaking wells and oil and gas infrastructure (not shown). | Hammack et al. 2016. *Methods for Finding Legacy Wells in Large Areas*, NETL-TRS-6-2016; EPAct Technical Report Series, National Energy Technology Laboratory, p 28

When all else fails, problematic wells must be remediated. This process is expensive and, in the case of abandoned wells, extremely difficult. The simplest approaches involve a "cement squeeze" in which cement is injected through perforations in the casing to provide a seal [Todorovic et al. 2015]. This process can be challenging either because the leaks are difficult to locate, or because the leakage pathways are too small or complex to be sealed by cement. A variety of innovative remediation approaches have recently been developed, including microbial methods [Cunningham et al. 2013] and various other polymeric sealants [e.g., Genedy et al. 2017]. In a worst-case scenario, a relief well can be drilled to intersect the problem well, as was done at Aliso Canyon [Conley et al. 2016].

More effective remediation strategies, in combination with monitoring, would significantly reduce risk by providing assurance that leakage processes can be stopped quickly and easily.

4.4.2 Scientific Challenges

Locating, evaluating and remediating existing and abandoned wells

Depleted oil and gas fields provide some of the most attractive, leading-use sites for CO_2 sequestration. They are well characterized, have proven caprock or geologic seals, and in some cases may be underpressured and capable of receiving substantial CO_2. In addition, these sites offer economic benefits in terms of aiding enhanced oil and gas recovery while sequestering CO_2, as recognized in DOE's Carbon Capture Utilization and Storage program. Unfortunately, these fields are likely to have many existing and abandoned wells, and strategies to minimize the risk of leakage from these wells are essential as part of a path toward gigatonne storage of CO_2.

Current logging technologies are inadequate, as they reveal limited information on casing and cement quality, cement placement, and bonding. They also do not adequately resolve the presence of small channels at well barrier interfaces (microannuli); leakage paths within cement (gas or liquid channels); or drilling-induced and natural fracture damage in the near-well rock. Logging also requires that operations be stopped, so continuous well monitoring is not currently possible. Improved logging techniques or improved log interpretation is therefore important for enhancing well integrity.

Enabling remote sensing for field-wide assessment of the location and leakage state of wells

Current technologies suffer from low spatial resolution or high thresholds for the identification of leakage in natural environments. Potential signals may show considerable natural variation in space and time, so ground-truthing and baseline values are required. As fluids leaking from wells at depth may reach the surface at considerable distances from well heads, and some depleted hydrocarbon fields include numerous wells, extensive areas must be monitored in an efficient manner. New air- land-, or water-borne methods should be developed for efficiently surveying larger areas, locating abandoned wells, and defining leakage states by direct monitoring of fluids or proxies near the earth surface. Signal processing of multi-parameter attributes and automatic image analyses is needed for fast, objective interpretation of remote sensing information to focus further targeted, ground-based investigations to attribute and quantify leakage fluxes.

Discovering low-risk techniques for interrogating state of wells, including casing, cement and near-well formations

Current logging technologies are inadequate to reliably assess well integrity, as they do not provide information at sufficient resolution regarding defects in and or along cement or in the nearby rock formations. The goal of more advanced well integrity monitoring, which is preferably continuous and remote, gives rise to several fundamental technological challenges:

- Efficient signal transmission: Which signals should be considered?
- Detection and enhancement of signals: Can new well construction methods simplify monitoring practices?
- Signal measurement and interpretation: Which signals correlate to well integrity issues?
- Installation of permanent instrumentation (sensors, tracer emitters, fiber optics): Can sensors be installed without compromising well integrity?

Identifying big data analytic approaches capable of assessing large data sets of digital well information

A wealth of data exist on well construction, operational conditions, geologic conditions, and fluid properties for the millions of wells that have been drilled in the United States and across the world. Data mining and machine learning technologies could enable full use of these records and their application to predicting well integrity. These approaches are flexible and can be combined with monitoring and predictive modeling capabilities to provide accurate assessments of well health in real time. Key results should include understanding the correlation between leakage rate and well properties.

Developing novel remediation and placement technologies

It is recognized that existing remediation technology is often inadequate and that new materials and methods of determining where and how to apply remediation technology are needed. One major challenge is to avoid a “blind squeeze” by improving techniques for determining where to place remediation materials and verifying the seal of the remediated well barrier. Plugged and abandoned wells present a much greater challenge, particularly since plugging practices are not always successful [White et al. 1992], and few remediation options are currently available. New remediation technologies should be measurable (where the remediation material goes can be determined) and verifiable (successful repair can be confirmed). The development of reliable, cost-effective remediation strategies would significantly reduce risk in CO_2 storage by providing confidence that problem wells can be repaired.

Establishing, demonstrating and forecasting well integrity

The future of CCS will require forecasting well integrity to facilitate long-term performance assessment and a confident end to monitoring activities at the end of project life. Wells constructed today are not designed for long-term isolation of CO_2. Laboratory and field measurements are needed to determine downhole conditions and material response as part of developing the ability to simulate the lifetime performance of wells. Novel technologies are needed, including more robust materials that provide self-sealing behavior and contain self-diagnosing monitoring systems.

Validating processes and fundamental relationships through field and bench-scale laboratory tests

The basis for developing fit-for-purpose materials and a predictive understanding of well integrity lies in improving the knowledge of stress in the well. Laboratory and field experiments are needed that determine downhole conditions, including the initial stress state of the wellbore system, the magnitude and impact of thermal and mechanical stresses, and the results of coupled processes that allow CO_2-bearing fluids to react with and chemically degrade well integrity. We need to understand the conditions under which the casing-cement-caprock system is capable of self-sealing through precipitation, scale formation, and plastic deformation of cement or caprock. Field tests that connect the well state with the leakage rate would provide much needed baseline data. Further, under what conditions are CO_2-resistant cement or steel needed and what properties must these materials have? Finally, the very long-term (hundreds of years) behavior of wells is largely unknown (e.g., what happens to cement and steel on these time scales). Accelerated testing standards are needed that predict long-term performance by extrapolating short lab-bench experiments to decades.

Integrating theoretical and experimental approaches to demonstrate long-term performance characteristics

The end-goal of understanding the fundamental behavior of wellbore systems is the development of high-resolution, high-performance simulation techniques that accurately capture multiscale, coupled thermal-hydrological-mechanical-chemical processes governing well integrity. These simulations should serve as the basis for risk analysis that adequately addresses gaps in knowledge and yields statistical confidence in well performance.

Developing sensor technologies to enable performance monitoring of wells

New sensor technologies are needed that continuously interrogate and diagnose well integrity issues. These could take many forms, from new wireline systems to embedded sensors, optical fiber, stress-reporting materials, “lab-on-a-chip” style devices, gas/liquid detectors, and corrosion sensors. They should include efficient, low-power communication methods that allow wireless, autonomous, or remote data transmission. Other approaches could include the development of slimhole monitoring wells and auxiliary functionality for downhole equipment such as packers.

Developing and qualifying smart materials for well integrity

New developments in material science have created opportunities for the application of smart materials with desirable properties that adapt to the downhole environment, report on downhole conditions, and/or self-repair damage. Self-diagnosing and self-monitoring functions are used, for example, in piezoelectric ceramics, shape-memory alloys, and optical fibers. Materials with tailor-made properties that allow signal detection through tubing (e.g., via contrast agents, stress-sensitive materials) can enhance well monitoring. Self-sealing materials could respond to the presence of CO_2, fractures, fluid flow, and other issues and release chemical sealants [Wu et al. 2012]. Alternative materials to CO_2-susceptible steel pipe or Portland cement could provide greater long-term performance.

4.4.3 Why Now?

Expectations for long-term well performance and the capacity of wells to withstand high-stress environments have evolved. Problems with old, plugged, and abandoned wells have perhaps been obscured by the fact that decommissioned oil and gas reservoirs are both pressure- and hydrocarbon-depleted at the end of use and are unlikely sources of pollutants, regardless of well condition. A new conceptual framework treats reservoirs as multi-use resources for the storage of waste and for the recovery of valuable commodities that future technology may make available, such as residual hydrocarbons or the metal content of brine. With multiple uses in mind, legacy wells should not be an economic or practical hindrance to reservoir development in the same way that development of carbon capture and storage is hindered by the problem of dealing with old wells. Recent technological developments in big-data analytics, sensors, telecommunication, and smart, built-for-purpose materials create new opportunities to reimagine what a well is and what it can do. Research investment now will bring down the costs of implementing new technology, given the recognition that the inherent value of reservoirs justifies expenditures now to maintain the potential for future use.

4.4.4 Conclusions

Gigatonne storage of CO_2 will require thousands of new injection and monitoring well installations. Storage reservoirs will inevitably encounter thousands and thousands more existing wells. The future success of carbon capture and storage necessitates the development and application of well integrity technology to (1) locate abandoned wells; (2) assess the integrity of abandoned, existing, and purpose-built wells; (3) detect and quantify leakage from wells; (4) compute downhole stresses and impacts on integrity; (5) predict the long-term performance of wells; and (6) develop cost-effective strategies to remediate leakage from abandoned and operating wells.

4.5 Carbon Dioxide Storage Priority Research Directions

4.5.1 PRD S-1: Advancing Multiphysics and Multiscale Fluid Flow to Achieve Gigatonne/year Capacity

Carbon dioxide storage is a proven technology with many large-scale projects in operation. However, to meet the required global scale-up of CCUS as a key method of limiting CO_2 emissions, an increase in CO_2 storage to the Gt/year scale is needed over the coming decades. Advances in understanding of multiphysics and multiscale fluid flow—resulting from laboratory analyses, computational methods, and field validation studies—should enable this scale-up. The key objectives of this PRD are to significantly improve storage efficiency and decrease long-term migration of CO_2 via step changes in understanding of the physics and chemistry of subsurface CO_2 flow at scales ranging from nanometers to kilometers. Making the best use of available storage sites by maximizing local storage capacity requires controlling the CO_2 plume using knowledge of local geology and physical processes. This will contribute to increasing the total storage capacity, which is also limited by the permissible pressure increase (see PRD S-2), and will improve the safety and security of CO_2 storage.

Over the past few decades, a growing number of CCS projects have steadily tested, demonstrated, and optimized the technologies involved in injecting CO_2 into geological storage units to reduce emissions to the atmosphere. Carbon capture and storage were first implemented at industrial scale at the Sleipner project in Norway in 1996 [Baklid et al. 1996], and by 2017 there were 21 large-scale CO_2 injection projects in operation [GCCSI 2016]. The current capacity needs to increase significantly if the greenhouse gas reduction goals embedded in the Paris agreement are to be realized [IEA 2016]. This CCUS scale-up challenge will require increases in both the number of projects and the capacity per project. This PRD addresses the fundamental scientific progress needed to enable storage at the Gt/year scale.

Scientific Challenges

Carbon dioxide injection into a subsurface brine-filled aquifer is essentially a two-phase flow problem. The CO_2–brine fluid pair is usually immiscible, and injection of CO_2 mainly follows a drainage process with an unstable mobility ratio that is understood based on experience in enhanced oil recovery projects. However, as CO_2 migrates in the rock formation, both drainage and imbibition flow cycles may follow; and a set of geochemical reactions between CO_2, brine, and mineral surfaces will occur. Using an analytical approach [Nordbotten and Celia 2006] and insights from field observations [Furre et al. 2015], it has been shown that CO_2 in the subsurface will typically be distributed with a “curved inverted cone geometry” (Figure 4.12). The detailed shape of the CO_2 plume and resulting saturation, and therefore the efficiency of the process (i.e., storage capacity), are strongly controlled by the fluid mobility, the viscous/gravity ratio, and the geological architecture. (See the sidebar “Multiscale CO_2 Flow Processes.”)

For the ideal case of injection in a horizontal layer with no pressure limitations (an infinite boundary condition), around 25% of the storage volume could in theory be used, assuming a viscous-dominated flow regime. However, the effects of fluid buoyancy (gravity forces) decrease the actual storage efficiency to the range of 1–5% [Okwen et al. 2010]. In the case of the long-running Sleipner CO_2 injection project (see Figure 4.4 in Storage panel report), seismic imaging was used to quantify the spatial distribution of the CO_2 plume and to estimate the actual fraction of the pore space used at around 5% [Eiken et al. 2011]. The presence of multiple shale layers in the Utsira sandstone formation has caused additional spreading and trapping of CO_2 with a storage efficiency that is higher than would have occurred in a homogeneous sandstone. Actual realized storage efficiencies are therefore controlled by the interaction of the fluid migration process (flow physics) with the geological architecture (reservoir heterogeneity). Although the effects of gravitational fluid segregation tend to reduce storage efficiency, geological structures and heterogeneities may increase efficiency, with structural traps providing secure long-term storage. The storage efficiency of a structural trap is on the order of 0.8, assuming a fully saturated trap minus the pore volume occupied by irreducible water saturation.

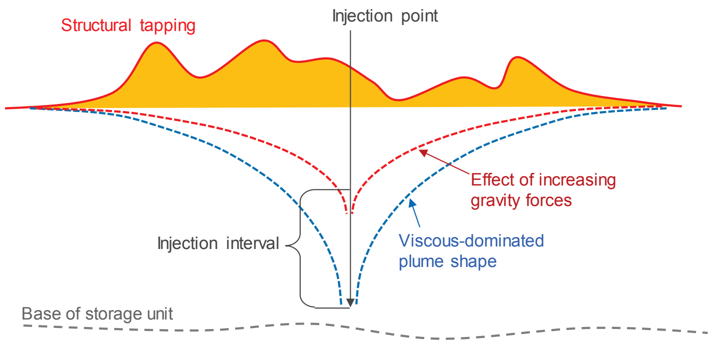


Figure 4.12. Sketch showing how gravity and viscous forces influence the CO_2 storage processes in a geological unit | Image courtesy of Philip Ringrose

Multiscale CO_2 Flow Processes

Physicochemical processes operating at various scales that combine to control the time scales and outcomes of CO_2 migration and trapping

10^{-4}	**Pore scale fluid dynamics**
10^{-3}	**Interfacial areas and chemical transport—controls on dissolution and water–rock chemical reaction**
10^{-2}	**Continuum properties**
10^{-1}	**Relative permeability, residual trapping, multiscale pore structures and capillarity**
10	**Sedimentary rock fabric and geologic structures**
10^{1}	**Capillary heterogeneity, laminations, bedding**
10^{2}	**Gravity currents**
	Convective dissolution
	Percolation vs. Darcy flow

In addition to the physical processes controlling CO_2 as a mobile phase, the following are important processes and trapping mechanisms to be considered:

- Residual trapping, whereby a migrating CO_2 plume leaves a trail of CO_2 trapped by capillary forces in pores and upstream of heterogeneous rock textures like laminations (for simplicity, both pore-scale residual trapping and capillary heterogeneity trapping are included in this term)
- Solubility trapping, whereby dissolution of CO_2 in brine (controlled by diffusion and convection) gradually transfers a portion of the CO_2 to the brine phase
- Mineral trapping, whereby a fraction of the mobile or dissolved CO_2 forms mineral phases, mainly by forming carbonate minerals.

When structural trap capacity is exceeded, lateral migration of CO_2 will occur, leading to further residual trapping along migration pathways. However, continuing long-term migration of CO_2 toward sensitive areas (e.g., protected groundwater, or any other subsurface resource) is undesirable and will lead to larger monitoring requirements and costs.

As initially proposed in the International Panel on Climate Change special report [Metz et al. 2005], these CO_2 trapping mechanisms will work over time to increase storage security in the long term. However, there remains considerable uncertainty around quantifying the efficacy of each process for any particular geologic reservoir, and a lack of knowledge regarding how to optimize injection strategies to make the best use of the available pore space.

The essential motivation for this PRD is to determine how researchers can better forecast, quantify, and optimize CO_2 storage efficiency.

More specific goals of this research objective are to

- Evaluate the contributions of different physical processes (e.g., advection, dispersion, dissolution) in controlling CO_2 storage efficiency
- Assess the contributions of multiple physical processes across multiple scales, inclusive of the interplay with natural geological heterogeneity
- Investigate ways in which knowledge of dynamic fluid processes can be used to optimize storage at a given site based on detailed multiscale geological architecture

New developments in observational and computational analysis are needed to construct rigorous models of macroscopic multiphase flow, permeability, and trapping consistent with pore-scale fluid dynamics. Currently, there are limited observations of properties controlling fluid–solid and fluid–fluid mass transfer during fluid flow within porous and fractured rocks. Continuum models for simulating these processes at reservoir scales remain too uncertain. Significant development is required, both in the observation of controlling pore-scale processes and the reformulation of upscaled models, before the models can achieve useful levels of predictive capability.

Research Directions

To address these challenges, we propose that significant advances in research on multiphysics and multiscale fluid processes involved in CO_2 storage will provide a basis for

- Improving the knowledge base of CO_2 storage concepts
- Significant steps in learning how to maximize CO_2 storage

Specific research activities will be focused at different scales within this system, leading to a set of more specific research questions:

- How does CO_2 migrate at the pore scale (nanometer to millimeter scale)?
- How do gravity, viscous, and capillary forces influence CO_2 migration at the rock-unit scale (centimeters to tens of meters)?
- Can introduced engineered nanoparticles favorably modify flow, saturation, and trapping?
- How will different storage unit architectures influence near-well storage efficiency?
- How can we use novel injection strategies to exploit geological heterogeneity, leading to optimized storage projects and higher overall efficiencies?

Note that this PRD with a focus on fluid flow is complemented by a second PDR focused on pressure. Recent advances in laboratory methods for microscale imaging of two-phase flow in porous rock media, including the possibility for time-lapse imaging of dynamic processes, demonstrate the potential for progress in this field (Figure 4.13) [Reynolds et al. 2017]. By imaging the CO_2–brine flow behavior through permeable sandstones under subsurface reservoir conditions, it is possible to quantify the in situ flow processes, leading to much improved estimates of CO_2 mobility and residual saturation.

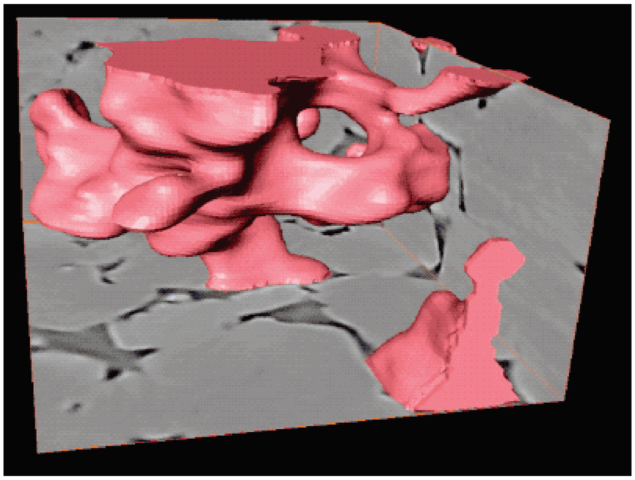


Figure 4.13. Recent insights from pore-scale imaging of fluid dynamics involved in CO_2 storage. Volume renderings of N_2 ganglia in a 720 × 720 × 360 µm volume are used to illustrate dynamic fluid connectivity | Reynolds et al. Dynamic fluid connectivity during steady-state multiphase flow in a sandstone. *Proc. Natl. Acad. Sci.* **114**(31), 8187–8192.

Advances in computational methods and high-performance computing (HPC) need to be applied to solve complex flow problems. Multiscale modeling frameworks (e.g., adaptive meshing and mesh refinement, hybrid percolation-Darcy simulators) are needed to incorporate the physical processes from the pore scale, through multiple-scale transitions, and up to the field and subbasin (multi-project) scale (see the sidebar "Applying High-Performance Computing to Multiscale and Multiphysics CO^2 Storage Problems"). Field validation of upscaling frameworks is needed, allowing more predictive modeling for long time scales (hundreds of years).

Concerning the novel injection strategies that might be used to exploit these improvements in understanding flow processes at the pore scale, a new generation of purpose-specific carbon capture and storage wells are anticipated that include long-reach horizontal, multi-branch, or vertical wells with zone-control systems. With new advances in well technologies, CO_2 projects will be able to design injection systems that allow optimal storage at specific sites. For example, Nazarian et al. [2013] showed a range of examples where modified injection strategies could lead to more efficient storage. Using models from existing projects at Sleipner and Snøhvit, they simulated cases with improved storage performance against the actual project metrics (Figure 4.14). This aspect of storage optimization is strongly linked to PRD S-3.

Applying High-Performance Computing to Multiscale and Multiphysics CO_2 Storage Problems

What will CCS actually look like in a full-scale geologic setting and mature commercial environment? It will progress only if we can reconcile understanding at both the very small and very large scales that CCS requires—analogous to how an understanding of particle physics informs the cosmos. Carbon dioxide storage is inherently a multiscale problem. Geologic and fluid dynamic processes from the molecular scale to the scale of large sedimentary basins must be assessed. New imaging technology at the microscopic scale (e.g., synchrotron imaging, focused ion beam, x-ray CT) and geophysical (seismic) imaging at large scales is dramatically changing the ability to visualize and understand fluids in complex rock media.

Scale	Units	HPC
Pore	Nanometer to decimeter	10^7 to 10^9 voxel models Highly parallelized
Field	Decimeter to kilometer	10^7 to 10^8 cell models 100s to 1000s of CPUs Uncertainty handling via multiple realizations
Basin	10s to 100s km	10^8 to 10^{10} voxels Multi-models/data sets Parallelized

Further progress at these disparate geologic scales will develop most rapidly with focused engagement of high-performance computing (HPC). CCS has arrived at a fortuitous moment, when data sets at disparate scales are becoming more widely available within both industry and research communities. At small scale, it is now fairly common to encounter pore-scale (micron) imaging resolution at core scale (decimeters). At this scale, multi-phase flow processes can be simulated with increasing accuracy and are being extended from nonreactive flow models into coupled models incorporating geochemical and geomechanical responses with associated uncertainties. The ability to visualize, simulate, and understand flow at these resolutions is on the verge of major breakthroughs. At large scales, researchers are now building high-resolution geologic data sets that cover thousands of square kilometers, hundreds of wells, and similar numbers of faults over kilometer-scale stratigraphic intervals.

These multiscale and multiphysics approaches, along with advances in HPC, are expected to result in significant steps in addressing the challenges of gigatonne CO_2 storage. HPC resources can be used to attack questions that were always considered important but could not be pursued meaningfully because of inadequate data, models, and computational power. In turn, it is unknown what impacts the pursuit of CCS will have on HPC, but it is very probable that new needs unique to CCS will present opportunities to develop new techniques (or modify existing ones, such as medical imaging) that can be advanced further as a consequence.

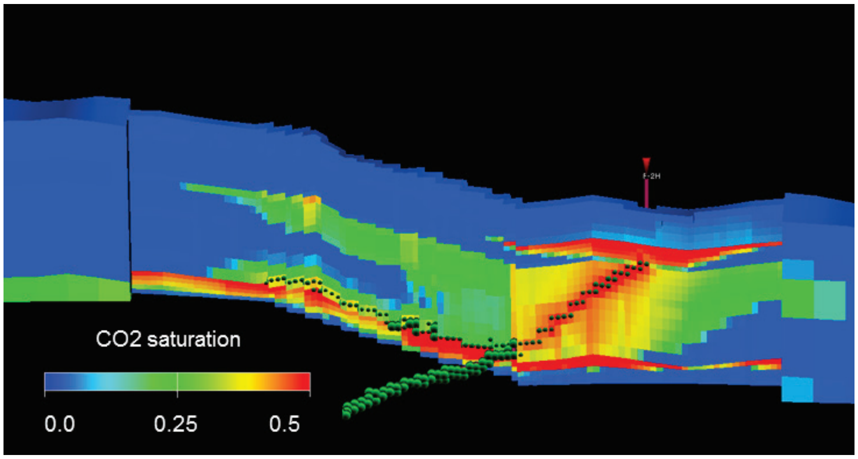


Figure 4.14. CO_2 plume resulting from an extended-reach multi-branch well after about 20 years of injection in a model based on the Tubåen storage units at the Snøhvit injection site. Vertical scale is exaggerated by 7. | Modified from B. Nazarian et al., Reservoir management of CO_2 injection: Pressure control and capacity enhancement. *Energy Procedia* **37**, 4533–4543. Copyright 2013 from Elsevier

Technology Impacts

The principal motivation of this PRD is to take current CO_2 storage technology (single-well projects at the 1 Mtpa level) to the 10–100 Mtpa level (via multi-well projects). To realize this goal, technologies will be sought that could double or triple near-well storage efficiency relative to the current benchmark of <5% use of the pore space. New insights into the physics and chemistry of CO_2 storage at in situ reservoir conditions could lead to significant improvements in storage efficiency using optimized CO_2 injection strategies and pressure management. Recent advanced well technologies applied in the oil and gas industry could be adapted and further developed to provide CO_2 storage–specific injection well solutions.

This knowledge could also potentially enable the extension of CO_2 storage into new geological domains, including low-permeability rock media, rock units with multi-pore dual-permeability architectures (e.g., fractured carbonates), residual oil zones, and novel CO_2 enhanced oil recovery schemes.

4.5.2 PRD S-2: Understanding Dynamic Pressure Limits for Gigatonne-scale CO_2 Injection

Gigatonne/year injection of CO_2 into basins around the world will entail regional pressure rise, the large-scale limitations of which are not well known. To avoid cap rock failure by fracturing, leakage through wells, and unacceptable levels of induced seismicity, better understanding of hydro-geomechanical processes from grain to reservoir scales is needed. Laboratory, field, and theoretical studies of the behavior and properties of cap rock and reservoir rock under dynamic pressurization histories will illuminate storage failure limits under in situ stress conditions. From this research program, forecasts of dynamic pressure limits for storage basins with large projected capacities can be developed, along with defensible strategies to mitigate negative impacts of storage-complex pressurization.

Scientific Challenges

Gigatonne CO_2 storage requires initiating many individual storage projects over multiple sedimentary basins around the world. Within each sedimentary basin, large aquifer systems or collections of systems are needed to serve as storage complexes. Multiple simultaneous injection projects in the same aquifers or depleted hydrocarbon reservoir systems will invariably lead to significant stratigraphic pressure increases, similar to those seen during geologic basin evolution during subsidence but over an essentially instantaneous time scale. Pressure plumes among neighboring projects will interact and combine to form a regional pressure footprint that is 10–100 times larger than any of the individual CO_2 plumes (Figure 4.15), as forecast by Nicot. [2008], Zhou et al. [2010], and Zhou and Birkholzer [2011]. In many different geological settings, it has been shown through modeling that accounting for these overpressures will generally restrict the ultimate CO_2 storage capacity at aquifer scale, even when a pressure management strategy is implemented [Bader et al. 2014; Thibeau et al. 2014; Gorecki et al. 2015].

As time goes on, the pressure plume will continue to evolve and move outward into the far field, possibly encountering weak points/shallow zones of the lower cap rock that are more sensitive to hydrologic and geomechanical impacts of pressure than the deeper injection zones. Pressure propagation to weak points may occur decades after the end of injection. As pressure increases, wells (abandoned or not) may not be able to sustain the rising pressure; wells will leak [Gasda et al. 2004; Birkholzer et al. 2011], and cap rock and faults may not be able to maintain their sealing capacity. Intact cap rock may begin to fracture if the minimum compressive stress is exceeded, and fractures may occur [e.g., Saltiel et al. 2017] or faults may activate seismically or aseismically [e.g., Guglielmi et al. 2015] and become more permeable. These processes are distinct from fracturing within the reservoir, which is often viewed as favorable for increasing injectivity and which can be controlled through monitoring and smart well management.

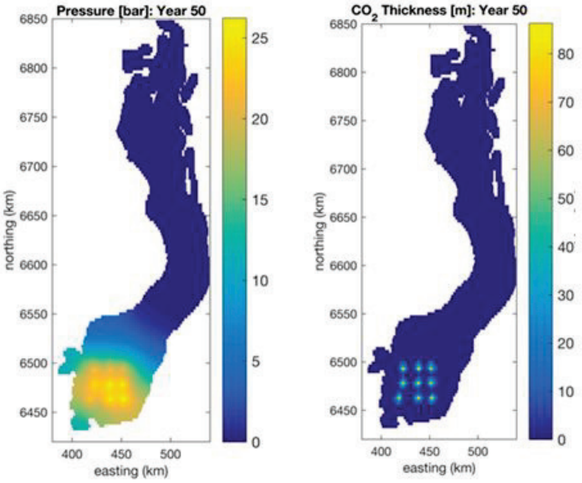


Figure 4.15. Pressure (left-hand side) and CO_2 plume thickness (right-hand side) for CO_2 injection into the Utsira after 50 years of injection at a rate of 100 Mtonne/year, showing the large pressure propagation relative to CO_2 plume migration. | Gasda et al. Investigation of caprock integrity due to pressure build-up during high-volume injection into the Utsira formation. *Energy Procedia*, **114**, 3157–3166. Copyright 2017 with permission from Elsevier

The need for gigatonne-scale CO_2 injection and the known hydrologic and geomechanical hazards of pressurization for geologic carbon sequestration integrity motivates the question: What are allowable and acceptable reservoir- and basin-scale pressure rises for the dynamic CO_2 injection processes? To answer this question adequately, we need to consider the properties of the overburden/underburden, which are typically not well characterized as a result of historic hydrocarbon exploration and production.

Cap rock failure can occur through a variety of processes, including cap rock hydraulic fracturing, reopening of fractures in an existing fracture network, reactivation of a fault that crosses the cap rock, or creation of permeability in the fault gouge. These processes will depend on rock properties—whether the rocks are more ductile or more brittle (see Figure 4.16), rock heterogeneities, the presence of natural and induced fractures, and faults.

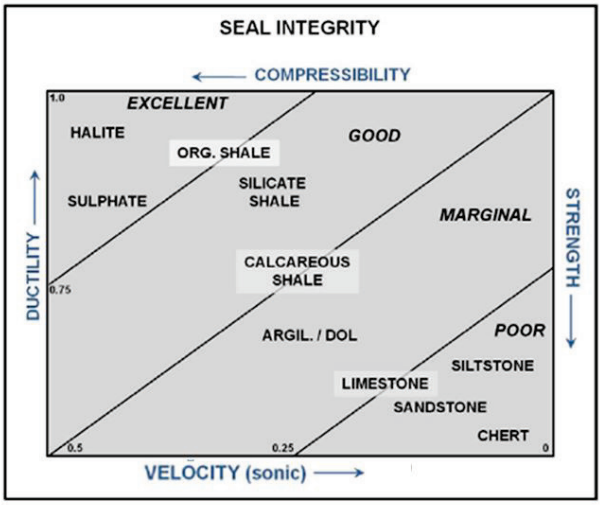


Figure 4.16. Qualitative plot of relative ductility and strength (vertical axes) versus velocity and compressibility (horizontal axes) for various lithologies, along with general quality of cap rock from a geological carbon storage perspective superimposed as diagonally oriented fields of excellent, good, marginal, and poor. | Modified from Oldenberg et al. 2017. *Recommendations for Geologic Carbon Sequestration in California: I. Siting Criteria and Monitoring Approaches, II. Example Application Case Study*. Lawrence Berkeley National Laboratory

Therefore, there is a need to understand fault internal structure and natural fracture networks and to be able to forecast permeability evolution under changing effective stresses. Knowledge of the in situ stress field is critical in modeling fracturing and induced seismicity processes. Quantification of initial (pre-injection) stresses is often based on a simplifying assumption that stresses vary with burial (or depth), even though rock heterogeneities, pore pressure variations, and faults are known to generate stress perturbations. Rapid pore pressure changes induced by the storage operations will also generate stress changes in the storage formation itself and in the surrounding formations.

Finally, the creation of a leakage pathway following a cap rock or fault failure implies a combination of multiple processes at various scales, ranging from a local failure initiated at grain scale, to its upward propagation into shallower formations—which implies coupling among local heterogeneities, effective permeability changes, fluid migration, pore pressure rise, and stress changes. On the other hand, some processes may limit the brine or CO_2 leakage because of changes in the bulk properties of the cap rocks or geochemical impacts on transmissivity along the leakage pathway(s). More insight could be gained by merging experience in natural hydrocarbon migration with experience in unintended CO_2 migration.

The process of fracture formation due to increasing pressure has characteristic behavior (e.g., Figure 4.17) that can be evaluated and measured using laboratory and in situ field tests. The typical field development practice would be to measure fracture pressure limits using such tests before commencing field operations. With improved understanding of the geomechanical properties and the pressure limits, future CO_2 injection projects may be able to control dynamic pressure evolution to avoid exceeding critical geomechanical limits near injection wells and in the far field.

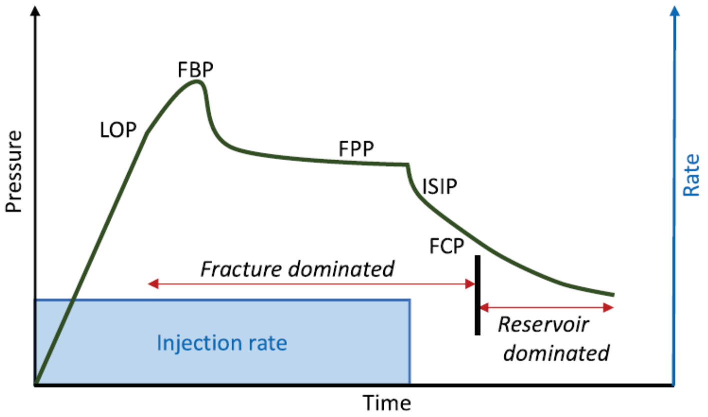


Figure 4.17. Schematic showing in situ fracture tests typical of the minifrac test procedure. LOP = leak-off pressure, FBP = fracture breakdown pressure, FPP = fracture propagation pressure, ISIP = instantaneous shut-in pressure, FCP = fracture closure pressure. Fracture-dominated vs. reservoir-dominated flow regimes are indicated by arrows. | Redrawn from Bohloli et al. Determination of the fracture pressure from CO_2 injection time-series datasets. *Int. J. Greenh. Gas Con.* **61**, 85–93. Copyright 2017 with permission from Elsevier

An important research target is to develop improved methods to characterize and locate zones of mechanical weakness within the cap rock. This can be achieved by improved analysis of both well data and seismic data. Mechanical characterization at the near-well scale can be achieved using focused acquisition and analysis of drilling data and rock cuttings [e.g., De Block et al. 2014]. Potential zones of weakness in cap rocks can be identified using advanced seismic analysis methods such as diffraction imaging [Brethaut et al. 2017].

In summary, the challenge is to quantify allowable pressurization through better understanding of the effects of the dynamic stress field, fluid pressure history, faults and fractures, and reservoir/cap rock heterogeneities from grain to reservoir scales. The understanding of allowable pressure will enable development of effective and practical mitigation strategies.

Research Directions

To achieve better understanding of dynamic pressure limits needed for gigatonne/year–scale injection, research needs to be undertaken in several directions.

Cap rock and overburden characterization remains a challenge, as cap rocks have been studied in less detail than reservoirs. Full data integration is required to better characterize the reservoir rocks, the cap rocks, the pore pressure, and the stresses. Further research is needed to fully integrate and exploit all of the information contained in logs (e.g., density, sonic at various scales, well bore imaging), cuttings, cores, local pressure and stress measurements, drilling behavior (mud losses, kicks, well ovalization), and hydraulic well tests. In the absence of dual sonic and core logs, the analysis of cuttings allows approximation of the mechanical properties of the cap rocks by combining the cuttings' mineralogical mapping and nanoindentation [e.g., De Block et al. 2014].

Extrapolation of local information (lithologies, petrophysical and mechanical properties, and stress and pore pressure) to the aquifer and basin scales should be pursued through basin modeling and seismic studies. Basin modeling enables forecasting of the buildup of stresses and temperature during the sedimentation processes, their changes due to potential later fluid charging phases, the generation of faults and their possible nature, and characterization of and impacts on the stress field. Seismic data can be reprocessed to enhance seismic diffraction (instead of seismic reflection) to improve fault illumination in order to identify subseismic faults (e.g., Brethaut et al. 2017). Both the well and seismic data can be integrated to perform seismic inversion (acoustic impedance, shear impedance, and bulk density volumes) useful to extrapolate the geomechanical properties to the far field (P-wave velocity, S-wave velocity, Vp/Vs, Poisson's ratio, shear modulus, bulk modulus, and Young's modulus) (e.g., Justiniano et al. 2015).

Modeling rock behavior under varying stress and pore-pressure conditions remains a challenge because of the effects of rock heterogeneity and coupled dynamic processes. Researchers need to better understand elasto-plastic behavior (failure modes) of rock systems and their viscous behavior, along with associated fluid flow, and consequently to be able to avoid or mitigate cap rock and fault failure. Doing so requires further laboratory tests at subsurface stress and pore pressure conditions, and testing of various loading and unloading phases to identify failure and stress paths. These tests should also provide further knowledge in relation to triggering of acoustic emissions and, ultimately, earthquakes.

Finally, the application of high-performance computing (HPC) to fully coupled thermo-hydromechanical models can provide a platform for advances in the description and behavior of small-scale and large-scale discontinuities (faults and fractures) that will be needed as part of the effort to understand dynamic pressure limits. An opportunity now exists to engage geologists, engineers, and technical computing specialists (with carbon capture and storage [CCS] experience and beyond) and provide access to unprecedented data scales and computing power to understand the impacts of CCS at the basin scale through high-performance simulation at sufficiently high resolutions. A refocused HPC effort for CCS should expand beyond traditional reservoir simulation with an emphasis on subsurface pressure and saturation distributions to address the effects on regional hydrodynamics, pressure perturbations, modified stress fields, and deformation at the reservoir and basin scales.

Technology Impacts

Research on dynamic pressurization and its impacts on hydromechanical processes affecting CO_2 containment have the potential to generate new well-logging and well-measurement technologies, along with related interpretative and integrative modeling capabilities. In situ experiments and underground laboratory experiments on fault properties and their evolution under stress may allow the development of new fault-displacement tools and new fault-property measurement tools. The collective advances in technology in this research field are needed to support gigatonne/year–scale CO_2 injection; they also will impact other related research communities working on subsurface problems, as well as more fundamental Earth science disciplines (e.g., seismology, fluid rock interactions, and behavior of deeper crustal fluid-flow systems).

Conclusions

Critical to the deployment of CCUS at the gigatonne scale is better understanding of dynamic pressure limits in the entire storage complex. To achieve this scale of injection without compromising the cap rock, causing well leakage, or triggering unacceptably large earthquakes, detailed knowledge is needed of how cap rock fails under overpressure conditions, how wells fail over time, and how fracturing and fault reactivation (including aseismic slip) occur under dynamic conditions.

4.5.3 PRD S-3: Optimizing Injection of CO_2 by Control of the Near-Well Environment

Gigatonne/year–scale CO_2 injection is dependent on long-term reliable operation of injection wells. Better understanding of phase change and related solids precipitation, formation damage, and fracturing caused by CO_2 injection is needed to ensure injectivity in high–capital-cost wells. The first generation of CO_2 injection projects, along with the large-scale application of hydraulic fracturing in the oil and gas industry, has provided a foundation upon which a focused research program is to be started on the subject of management of the near-well environment for optimal injectivity. Research aimed at improved understanding of induced fractures (hydraulic and thermal) and other near-well treatments to enhance injectivity can be carried out by combined laboratory, theoretical, and field research, including the use of underground laboratories. Development of CO_2-specific additives and next-generation well technology to manage injectivity (including effects of formation damage) is another promising area. Finally, development of the underpinnings of the next-generation well technology to optimize injectivity in difficult reservoirs is to be explored to ensure continued improvements in injection projects. Research in these areas has the potential to lead to new technologies and services critical to the development of gigatonne-scale CO_2 injection projects.

Scientific Challenges

Carbon dioxide injection projects are dependent on the good design and reliable operation of injection wells. To ensure stable injection over tens of years, the various elements of the well (tubular members, cements, packers, and well casing) must be designed to operate under the pressure, temperature, and compositional (P, T, and X) variations expected over the life of the well. The injection interval may be completed as an open hole, but more commonly advanced formation-specific well-completion solutions are used (e.g., slotted liners, gravel packs, completion shots). The near-wellbore environment is likely to be affected by drilling mud invasion of the porous rock units and the effects of stimulated or natural fractures. The vaporization of water from the in situ brine due to injection of dry CO_2 may lead to precipitation of salts, and dissolved CO_2 in brine may lead to dissolution-precipitation reactions with mineral phases. In addition, injection of cold CO_2 can cause thermal fracturing. Some of these effects may be detrimental to CO_2 injection, while others may be beneficial. The motivation of this PRD is therefore to better understand important processes in the near-well environment that will lead to technical solutions for limiting detrimental effects and optimizing injectivity over the life of gigatonne-scale CO_2 injection projects. The large number of oil and gas extraction and related research projects worldwide that have used hydraulic stimulation provide a wealth of data on which advances in CO_2 injectivity control can be based.

With a growing body of experience from first-generation CO_2 injection projects, the research community is now in a position to start designing wells to give optimal performance and stable injection over the planned project lifetime (typically 25 years). Initial plans for an open-hole completion of the Sleipner injection well did not prove to be successful, and injection problems due to sand influx had to be solved by re-perforation of 7 in. high-chromium stainless steel tubing and installation of sand and gravel packs at the injection interval. Following this modification in the well design (in 1997), regular operations have continued for over 20 years with stable injection rates and pressures [Furre et al. 2017]. The modified successful well design from the Sleipner project is shown in Figure 4.18.

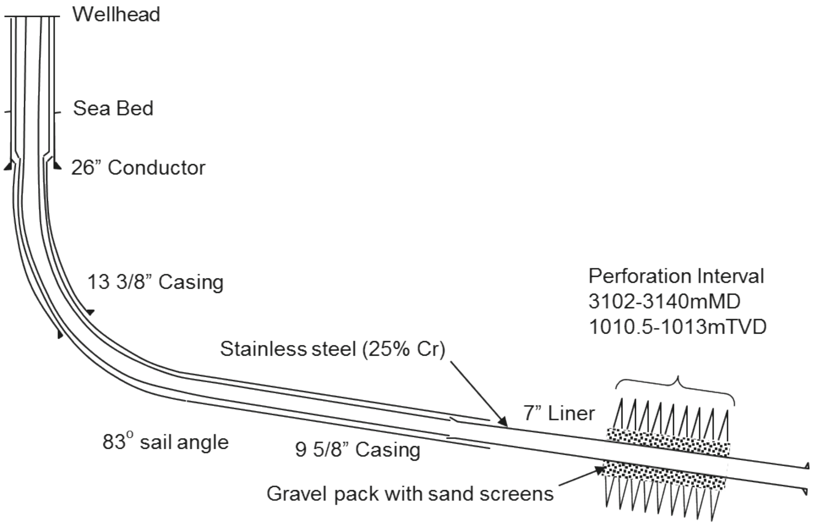


Figure 4.18. Key elements of the injection well design at the Sleipner project: long-reach horizontal well with a sail angle of 83°, perforated injection interval of 38 m with gravel pack and sand screens, high-chromium (25% Cr) stainless steel used for the 7 in. injection tubing and the exposed sections of the 9⅝ in. well casing. | Redrawn from Pawar et al. Recent advances in risk assessment and risk management of geologic CO_2 storage. *Int. J. Greenh. Gas Con.* **40**, 292–311. Copyright 2015 with permission from Elsevier

The Snøhvit CO_2 storage site (which started injection in 2008) also experienced irregular injectivity in the first years of operation (Figure 4.19). Initially, the irregularities were due to near-wellbore effects related to salt precipitation (e.g., Figure 4.20); but then, in later stages, a gradual rising trend in pressure was caused by the effects of geological flow barriers [Pawar et al. 2015]. A modified injection strategy was implemented in 2011, and since then more stable injection has been achieved.

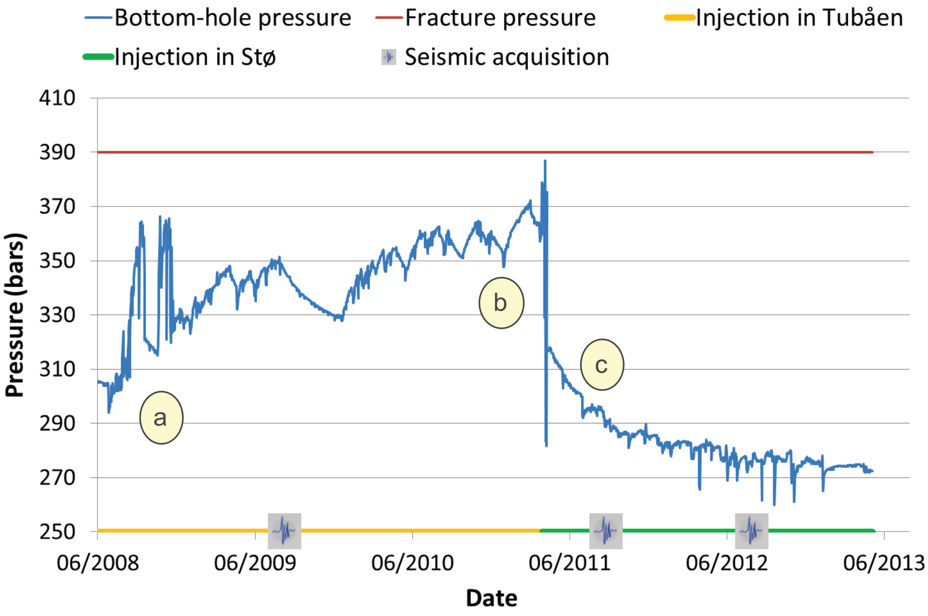


Figure 4.19. Pressure history at the Snøhvit CO_2 storage site (2008 to 2013) with time-lapse seismic acquisition surveys. Three main features of the injection pressure history are (a) early rise in pressure due to near-wellbore effects related to salt precipitation, (b) a gradual rising trend in pressure due to geological flow barriers in the Tubåen Fm., and (c) pressure decline to a new stable level following well intervention and diversion of the injection into the overlying Stø Fm. | Reproduced from Pawar et al. Recent advances in risk assessment and risk management of geologic CO_2 storage. *Int. J. Greenh. Gas Con.* **40**, 292–311. Copyright 2015 with permission from Elsevier

The most straightforward way to increase near-well permeability is to fracture the reservoir. Fracturing can be accomplished using high injection pressure, energetic materials (e.g., low-explosives), and thermal means. In most cases, CO_2 injection will involve significant heating of the CO_2 stream within the wellbore and into the rock formation. Conversely, injected CO_2 may cool the rock formations, potentially causing thermal fractures [Luo and Bryant 2011]. Stimulation of the reservoir by means of hydraulic, explosive, or thermal fracturing in the near-well environment may be beneficial (giving improved injectivity) or could be detrimental if fractures should propagate to threaten the integrity of the rock units. There is thus a critical need to better understand the development and nature of stimulated fracturing for controlling CO_2 injectivity.

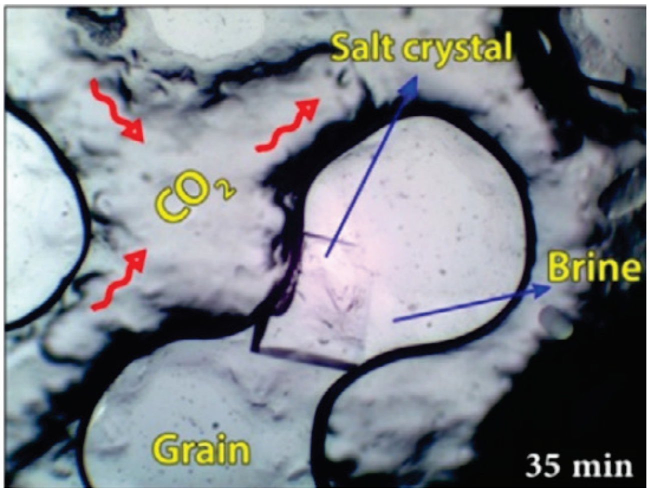


Figure 4.20. Formation and growth of a large salt crystal in a trapped liquid bridge for a CO_2-brine transport and reaction experiment. | Adapted from Miri et al. 2015. *Int. J. Greenh. Gas Con.* **43**, 10–21. Copyright 2015 with permission from Elsevier

Research Directions

The panel identified the following research directions as part of this PRD:

- Improve understanding of induced fractures (hydraulic and thermal) and other near-well treatments to enhance injectivity using combined laboratory, theoretical, and field research including the use of underground laboratories (e.g., the US Sanford Underground Research Facility or the Swiss Mont Terri and Grimsel laboratories).
- Develop CO_2-specific additives to manage the injectivity (including effects of formation damage).
- Develop a multiscale understanding, grounded in experimental studies, to connect molecular-, nano-, and mesoscale phenomena using advanced materials measurement characterization techniques with laboratory-scale measurements and field-scale observations.
- Develop chemo-morphological-mechanical understanding of accelerated carbonate conversion pathways and implications for well-bore integrity and gigatonne-level CO_2 storage.
- Develop the underpinnings of next-generation well technology to optimize injectivity in difficult reservoirs (e.g., tight and/or fractured carbonate reservoirs).

Technology Impacts

Research in this area will improve the understanding of how to manage injectivity across the range of high-capacity CO_2 storage reservoirs. The research developments in stimulation, additives, and wells have the potential to lead toward new technologies and services critical to the development of gigatonne/year–scale CO_2 injection. With a focus on materials technology and use of molecular-scale/nanoscale additives, this PDR will also have much common ground with CO_2 capture research and more fundamental aspects of the chemistry of materials.

4.5.4 PRD S-4: Developing Smart Convergence Monitoring to Demonstrate Containment and Enable Storage Site Closure

This PRD addresses the need to more directly detect and measure CO_2 in deep storage formations. There are a number of drivers for this requirement; but in summary, there is a need to demonstrate, during operation, that a storage site is behaving as expected and that long-term geological containment is being achieved. Monitoring provides the information that establishes convergence between actual site behavior and simulations of behavior over the long term—a fundamental requirement to enable site operators to close the site and transfer long-term liability to national authorities.

Scientific Challenges

Existing CO_2 storage projects have demonstrated the need for convergence monitoring to meet regulators' demands and satisfy public concerns regarding project safety. Monitoring is also necessary for the location, attribution, and quantification of the CO_2 plume, including the assurance that CO_2 leakage has not occurred. Moving from the megatonne to the gigatonne scale in storage will require much larger monitoring networks that cover larger areas over longer injection times. At gigatonne scales, direct and/or indirect conformance measurement will be temporally and spatially discrete and costly. Fine spatial resolution and high temporal frequency are currently needed and subsequently may require regular or continuous monitoring capabilities. In addition, as plumes evolve from the near- to far-field, the measurement type, frequency, and resolution will also change, resulting in additional uncertainty and complexity.

Research Directions

The key to addressing these challenges is to develop new tools and technologies to directly measure state variables and improve resolution in the far-field. To achieve these advancements, we propose four research directions:

1. Improve resolution in the far-field, including development of new tools to directly measure state variables
2. Improve tool deployment for smart monitoring in the far-field
3. Improve methodologies for monitoring conformance
4. Optimize interpretation of complex data sets

Table 4.2 shows a list of proposed research directions for meeting future project needs to acquire, validate, and integrate monitoring data that are at high resolution and are collected continuously and in real time.

A fit-for-purpose monitoring system contains those monitoring techniques that, when used together, produce the evidence for system performance with acceptable uncertainty. Such a monitoring system ideally avoids unnecessarily expensive or ineffective monitoring in large-scale storage projects. The monitoring system design is risk-based, focusing on the elements that are considered to have the highest potential for anomalous behavior. The ability to assess the value of the individual monitoring techniques in reducing the uncertainty in site performance should also be developed.

Table 4.2. New tools and technologies for smart convergence monitoring

New nanoparticle-based technologies for illuminating the far-field
New sensors for temperature, saturation, chemistry, pressure, density, conductivity, stress, and dynamic processes
New tools as alternatives to complement conventional indirect methods, including • Density and electrical methods • Stress and strain data • High-resolution distributed acoustic sensing deployed horizontally and offshore • Spontaneous potential • Raman scattering at suface and down-hole • Remote sensing • Density micro-electromechanical sensors • Muon detection • Resistance tomography • Magnetotellurics • InSAR GPS and tiltmeters • Microseismics via adaptation of fiber optic technology as a diagnostic tool

Technology Impacts

Transformative technologies developed from this PRD will provide more tools at lower cost with improved accuracy to enable commercial-scale carbon capture and storage deployment. Parallel benefits will include reducing risk through time, increasing confidence, expediting permitting, and providing social license for project operation, including site closure.

4.5.5 PRD S-5: Realizing Smart Monitoring to Assess Anomalies and Provide Assurance

This PRD describes goals for smart monitoring to detect anomalies in the operation of storage systems and to assess the causes and impacts of leakage. In addition to leakage, anomalies may include events that do not pose a threat of leakage but may lead to changes in the CO_2 storage system operation. Since anomalies result in material impacts, monitoring requires a strong methodology and an ability to quickly and robustly identify whether the range of data acquired is acceptable or indicates a threshold has been exceeded, triggering further action to assess or attribute the source of the variation.

Scientific Challenges

The CO_2 storage community had its first experience of responding to a public claim of leakage in 2011: farmers living near the IEA Greenhouse Gas Weyburn–Midale CO_2 Monitoring and Storage project (in Saskatchewan, Canada) alleged that CO_2 was leaking to the ground surface and impacting their land Beaubien et al. 2013; Romanak et al. 2014]. More recently, the offshore Tomakomai (Hokkaido, Japan) project underwent a regulatory suspension because he thresholds designed for the marine monitoring plan were exceeded [MOE 2017]. These experiences illustrate the importance of being able to quickly and accurately respond to concerns from regulators and the public. As CO_2 storage becomes widespread, more claims and concerns regarding potential leakage may be brought to light by the public, and workflows should exist for their assessment. Regulatory and competent authorities will also require projects to prepare and provide staged plans for review approval and implementation.

Research Directions

To address these challenges, four research directions are proposed:

1. Improve and develop methods of identifying, attributing, and quantifying anomalies
2. Develop risk-based techniques and methodologies for assessing the value of monitoring of anomalies
3. Develop staged monitoring programs and workflows
4. Develop/create smart monitoring systems

For assurance monitoring, anomalies must first be located and then attributed to a source to determine whether the anomalous signal results from storage operations or some other industrial or environmental cause. If the anomaly is attributed to leakage, quantification of the emissions will be required. “Controlled release” experiments, in which anomalies are created deliberately, suggest extensive tools and techniques that might be used to accomplish monitoring for successful field deployments. Table 4.3 shows proposed advancements in approaches and methods to identify and attribute anomalies and to quantify any emissions resulting from leakage at onshore and offshore storage sites.

Table 4.3. Recommended improvements to approaches and methods for anomaly assessment

Develop methods of identifying, attributing, and quanfying anomalies in all domains onshore and offshore
Ensure durability in harsh environments over long time frames
Develop advanced new tools for monitoring anomalies, for example, • Onshore and offshore stoichiometric-based/process-based techniques • Tracers • Multi-level pressure sensors with lifelong reliability • New sensors for pressure, temperature, chemistry (including hydrocarbons), pH • Economical field-based N_2 sensors • Wellbore integrity, including in situ autonomous real-time measurements of corrosion and leakage • Autonomous monitoring sensor vehicles • Advanced marine sensing, including acoustic bubble detection • Optical, laser, and spectroscopic methods

For source attribution, variability is a major issue to be addressed, because environments are known to be rapidly changing as shifts in land use, population growth, and climate change itself accelerate. Baseline-dependent methods, especially in the nearest-surface environments where variability is highest, are likely to create false positives for leakage—as happened at Weyburn with the Kerr Farm incident and at the Tomakomai project [MOE 2017]. Figure 4.21 shows two examples of baseline-independent methods: one a "bio-oceanographic" method of offshore storage [Uchimoto et al. 2017] and the other a process-based method of onshore storage [Romanak et al. 2012].

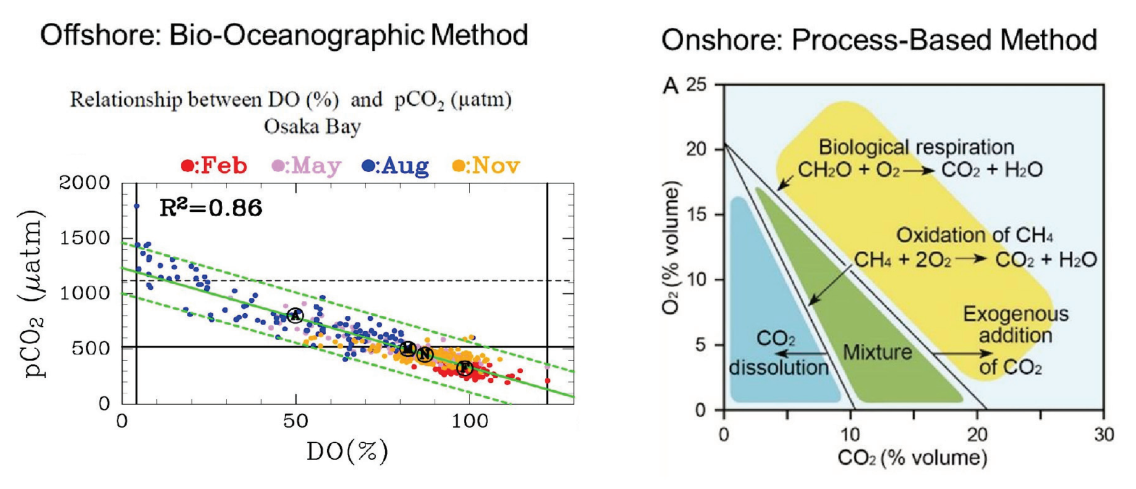


Figure 4.21. Examples of baseline-independent method for onshore and offshore storage projects. | Left: Uchimoto et al. A novel method to detect CO_2 leak in offshore storage: Focusing on relationship between dissolved oxygen and partial pressure of CO_2 in the sea. *Energy Procedia* **114**, 3771–3777. Copyright 2017 with permission from Elsevier; Right: Romanak et al. Process-based soil gas leakage assessment at the Kerr Farm: Comparison of results to leakage proxies at ZERT and Mt. Etna. *Int. J. Greenh. Gas Con.* **30**, 42–57, Copyright 2014 with permission from Elsevier

Current methods mostly rely on measurements of natural background or baseline CO_2 concentrations over 1–3 years (e.g., Schloemer et al. 2013). But baseline conditions measured at the beginning of a project will not represent baseline conditions throughout the lifetime of the project. Using a baseline concentration method will lead to many false positives and threaten public perception and projects. Quantifying "emissions apart from natural baseline," as many regulations require, is currently behind the research curve.

There is a practical need to develop baseline-independent methodologies, such as stoichiometric process-based approaches, in both terrestrial and marine environments. Methods that use tracers in new and innovative ways, and advanced marine sensing—for example, for acoustic bubble detection—are of interest.

Technology Impacts

The ability to identify and assess anomalous signals over multiple domains outside of the storage reservoir in both terrestrial and marine environments is critically important for environmental protection, stakeholder assurance, and compliance with regulations. It also provides the basis for activating staged monitoring programs and workflows that move the monitoring through full assessment to an acceptable outcome. With these advancements in place, methodologies for environmental assessments will be solid and dependable. They will increase public confidence, ensure environmental and stakeholder protection, and allow projects to move forward without complications or doubt, thus enabling Gt-scale storage.

4.5.6 PRD S-6: Improving Characterization of Fault and Fracture Systems

This PRD addresses the following questions. How can we make breakthrough advances in our ability to detect, map, and characterize faults and fractures, both within target reservoirs and in surrounding rocks—especially critically stressed faults within underlying crystalline basement rock? How can we map the stress field around faults? How will long-term exposure to CO_2 flooding affect fault properties?

Scientific Challenges

One of the first steps in assessing the potential seismic risk for a storage site is to identify faults that might be capable of producing damaging seismic events. This task, as well as distinguishing hazardous from nonhazardous faults, remains a challenge for existing geophysical techniques. Moderate-size faults pose the greatest challenge, as they are capable of generating damaging events yet are sufficiently small that they are difficult to detect via traditional means, especially when they are located within crystalline basement rocks. The challenge becomes readily apparent when recent case studies of induced seismicity are considered: the faults on which seismicity occurs are typically not visible before being reactivated by injection (see the example shown in Figure 4.22 [Diehl et al. 2017]). If researchers cannot image faults, then they cannot quantify the seismic hazard the faults pose.

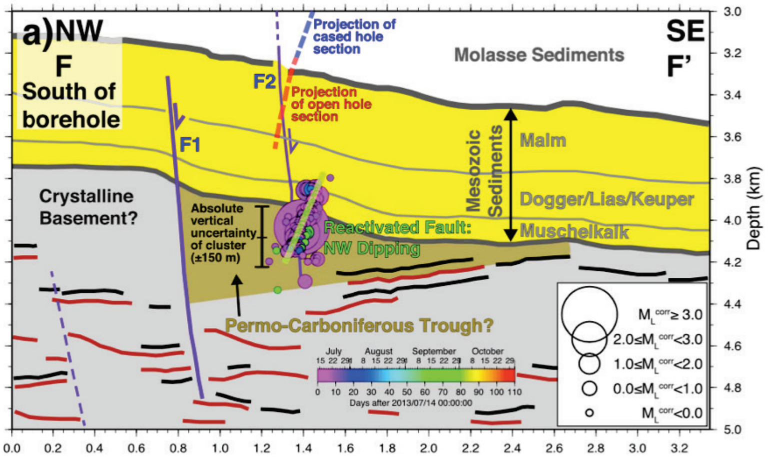


Figure 4.22. Cross section showing seismic events induced by the St. Gallen geothermal project, overlaid on a schematic geological section based on a reflection seismic survey. The NW-dipping fault on which seismicity occurs was not initially identified by the survey, while other faults that had been imaged did not produce seismicity. | From Diehl et al. 2017

Moreover, only a subset of faults will be at or near a critically stressed state. Of these, some will lack rheological properties prone to dynamic fault rupture [e.g., Garagash and Germanovich 2012]. Therefore methods to image stress fields around faults must also be improved, as well as the understanding of the fault rheological properties that will control seismic slip under long-term CO_2 flooding conditions.

Reflection-seismic imaging is relatively mature technology; however, the imaging and characterization of basement faults has heretofore been a low priority for existing industries. The particular challenge posed by imaging basement faults, such as the absence of sub-horizontal reflectors offset by a fault, necessitates novel methods of fault imaging at depth. The development and application of other geophysical methods, such as high-resolution gravity and magnetic methods to image basement faulting [e.g., Shah and Keller 2017], will also be necessary.

The measurement of stress along wellbores is a standard technique [Schmitt et al. 2012], and regional stress data are readily available [e.g., Heidbach et al. 2016]. However, such measurements do not capture the local stress-field reorientations that can occur around faults and other structural heterogeneities, which could determine whether faults are near a critically stressed state. Methods are therefore required that are capable of extrapolating from sparse wellbore stress measurements to provide an accurate map of stress conditions at any point in the subsurface. The key to this challenge is the development of geomechanical models of stress conditions that are constrained not only by wellbore stress measurements but also by geophysical proxies for stress conditions, such as seismic anisotropy [e.g., Hall and Kendall 2003] and the source mechanisms of microseismic events [e.g., Al-Anboori and Kendall 2010]. Links between geomechanical simulations and geophysical proxies therefore require further development.

Passive seismic methods have also demonstrated the potential to characterize both faults and stress conditions. As acquisition costs drop (for example, using novel methods such as fiber optic distributed acoustic sensing) and computational resources increase, “large-N” (i.e., large number of acquisition points) arrays offer the potential for novel imaging of microseismic events. So does the use of tomographic and/or migration-based methods [e.g., Lin and Zhang 2016] to image subsurface structures and stress conditions.

The knowledge of fault rheological properties and the ability to image these properties in situ is not currently sufficient for determine, a priori, which faults may produce seismic slip, which may slip aseismically, and which are not prone to activation. Moreover, it is not know how long-term exposure to CO_2 flooding could affect these fault characteristics. This gap in knowledge speaks to the fact that the understanding of rupture nucleation and slip propagation is fundamentally lacking.

Research Directions

Research is needed that combines laboratory studies, mesoscale field experiments [e.g., NERC 2016], and full-scale case studies. In particular, mesoscale field experiments that replicate the expected conditions during CO_2 flooding into faulted reservoirs are essential. High-resolution monitoring of such field experiments has the potential to image rupture nucleation behavior, a process that remains poorly understood, and to reveal what field observations might enable us to characterize in situ fault rheological properties.

In upscaling to Gt storage sites, characterization of every individual fault will not be feasible. Instead, it may be more appropriate to develop methods for geostatistical characterization across a given region using, for example, field observations linked to basin-scale structural modeling. This approach would allow the identification of optimal areas for development, unfavorable sites that should be avoided altogether, and actions that might make suboptimal sites more favorable.

Technology Impacts

Developing the ability to image and understand faults would improve site characterization significantly, allowing the CCUS community to

- avoid unsuitable sites
- ensure that monitoring programs are appropriate in scale to the expected risk
- boost regulator confidence in proposed activities

Induced seismicity is a significant issue for a range of industries. Hence, developments in this field will have impact far beyond the CCUS industry. Indeed, improvements in our fundamental knowledge of fault behavior will have implications for the understanding of tectonic seismic activity in general.

4.5.7 PRD S-7: Achieving Next-Generation Seismic Risk Forecasting

This PRD address the following questions: What methods can we use to produce successful forecasts of earthquake hazard during injection? What are the controls on largest event sizes? Can seismic hazard be mitigated using proactive control measures?

Scientific Challenges

Forecasting seismicity remains a fundamental scientific challenge: the complex nonlinear system that combines the rheology, the stress state of faults, and the role and distribution of fluid remains poorly understood. The occurrence and severity of induced seismicity depend upon fluid injection parameters, the geomechanical condition of the reservoir, and the proximity and configuration of nearby geological structures. There are fundamental questions about which parameters control the timing and nucleation of fault slip, whether slip is seismic or aseismic, and how much slip may occur. These issues are important, as ultimately the areal fault extent and average slip determine the maximum magnitude of earthquakes.

A range of mitigation strategies exist for sites that experience induced seismicity, including

- Stopping or reducing injection
- Injecting into an alternative formation
- Managing pressure through brine extraction
- Dispersing injection
- Attempting to avoid hazardous faults
- Attempting to induce aseismic fault creep rather than seismic rupture
- Retrofitting vulnerable structures
- Modifying community engagement

However, traffic light system strategies do not provide a framework within which the potential efficacy of different mitigation strategies can be evaluated.

Models that are capable of forecasting seismicity produced by fluid injection are therefore required. Such models should integrate injection parameters and monitoring data in real time to characterize the evolving site conditions, thereby providing seismic hazard assessments over short-term (days, weeks) and long-term (months, years) time scales.

Models must also provide a framework for testing predictive scenarios, allowing an operator to compare the efficacy of various potential mitigation measures and to evaluate the scale of mitigation strategy required. For example, at a site experiencing problematic levels of seismicity, by how much might injection need to be reduced to lower the seismic hazard to an acceptable level? Conversely, at a site that has not experienced induced seismicity, by how much can injection be increased without increasing the seismic risk beyond an acceptable level?

Broadly speaking, seismicity forecasting methods fall into two categories: statistical models based on prior observations of seismicity [e.g., Van der Elst et al. 2016] and physical models that numerically simulate geomechanical processes occurring in the reservoir [e.g., Cappa and Rutqvist 2011]. Statistical models are typically quick and simple to deploy. However, concerns remain about their ability to capture the long-term evolution of a reservoir. Physical models require extensive site characterization work and must incorporate a wide range of complex, coupled processes (Figure 4.23). It may also be difficult to incorporate inherent geological uncertainties. Recent developments have sought to incorporate both statistical and physical modelling to create hybrid models, for example, by using stochastic parameterization to incorporate geological uncertainty into physical models [e.g., Verdon et al. 2015]. However, these methods are still limited by gaps in our understanding of the mechanics and probabilistic features of earthquake generation; they require further theoretical study, experimental results, and observations of past and ongoing earthquake sequences.

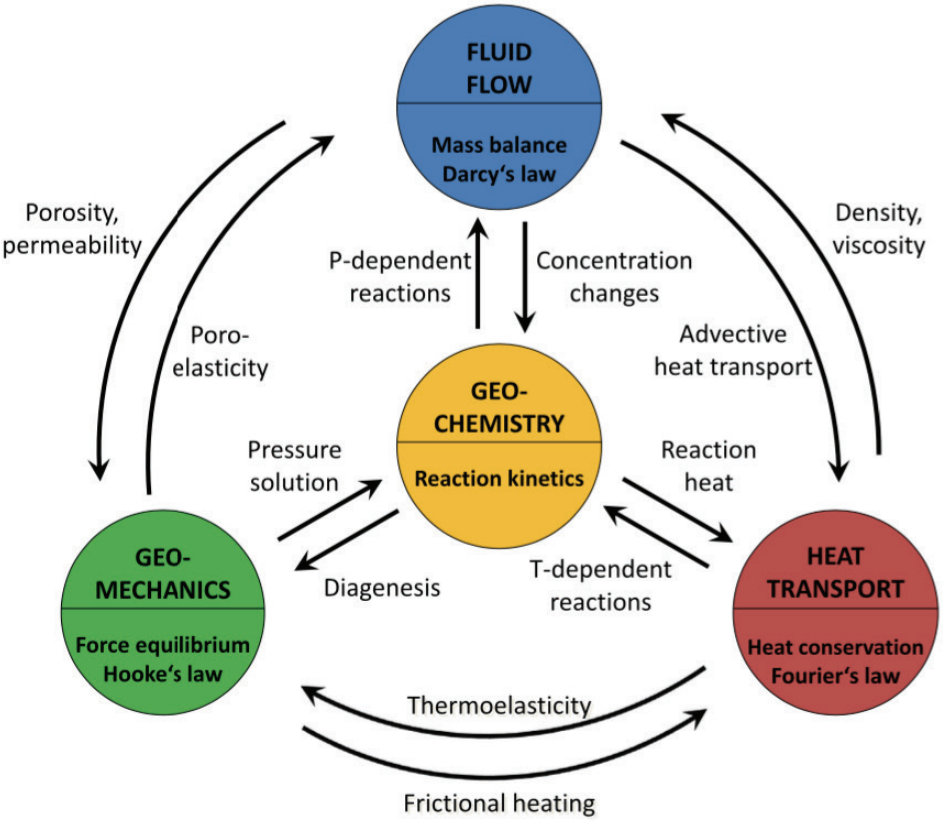


Figure 4.23. Schematic representation of the coupled thermo-hydro-mechanical-chemical processes relevant to injection-induced seismicity. | Reproduced from Gaucher et al. Induced seismicity in geothermal reservoirs: A review of forecasting approaches. *Renew. Sust. Energy Rev.* **52**, 1473–1490. Copyright 2015 with permission from Elsevier

Research Directions

Improvements in the ability to model induced seismicity are anticipated via a number of research avenues. Advances in machine learning methods [e.g., Käufl et al. 2016] offer the potential to improve statistical forecasting methods. Developing a better understanding of fundamental fault behavior will produce improvements to physical models. In particular, the availability of increased computational power will allow the incorporation of stochastic methods into physical modeling approaches. Rather than producing a single geomechanical model for a given reservoir, as is often the case at present, we should aim to produce suites of modeled scenarios (incorporating thousands of model instances), resulting in statistics-based probabilistic seismic hazard assessments derived from physical models. Only by doing so will it be possible to properly assess the impact and efficacy of the various potential mitigation strategies on seismic hazard at a given site. Although such approaches are common in other modeling communities (global climate modeling, for example), they are not commonly used for geomechanical simulations of induced seismicity.

For the science of induced seismic risk forecasting to progress, robust and independent model testing must take place [e.g., Kiraly et al. 2014]. Without such testing, it is impossible to properly assess which model types most accurately forecast seismicity [e.g., Zechar 2010] and thereby identify the necessary improvements to modeling strategies. For natural tectonic seismicity, a forum for model testing has been created, the Collaboratory for the Study of Earthquake Predictability (www.cseptesting.org). A similar international forum should be established to coordinate rigorous validation of proposed models against a large number of field data sets to build community confidence in their utility. Decision-making and management strategies based on probabilistic seismic risk assessments must also be developed so that model results can be effectively incorporated into site operation procedures/guidelines.

Technology Impacts

The research suggested in this PRD will contribute to better fundamental understanding of earthquake physics and statistics. The number of available case studies of induced seismicity, which can be used to validate novel model approaches, has increased rapidly in the past decade. Development of rational risk management schemes using all available data will support rapid but well-informed decision making. This will enable injection sites to avoid triggering events that, left unmitigated, could shut down a project.

4.5.8 PRD S-8: Locating, Evaluating, and Remediating Existing and Abandoned Wells

Cased-hole logging is performed to evaluate well integrity, and the logs are interpreted to deduce information regarding the sealing ability of barriers. Unfortunately, current logging technologies are inadequate, as they can reveal only some information on casing quality and cement placement and bonding. Little information is available on the presence of small channels at well barrier interfaces (microannuli) or leakage paths within the cement material (uncemented channels, bypassed pockets). The same is the case for damage in the near-well rock (drilling-induced damage, natural fractures). Improved logging techniques, or improved log interpretation, is therefore an important challenge for enhancing well safety. Logging also requires that operations be stopped, so continuous well monitoring is not possible. This requirement precludes condition-based intervention schemes, which would allow corrective and preventive measures to be implemented.

Tophole or remote well integrity assessment is currently not possible. As a result, old plugged and abandoned wells are typically treated as being high risk, so heavily drilled reservoirs are less attractive as CO_2 storage sites (despite the wealth of information available regarding the subsurface in such locations). Plugged and abandoned wells are cut several meters below surface to restore the site, and there is currently no way to enter them with logging tools, assess their leakage potential, or repair them if they are leaking. Enabling tophole or remote well integrity assessment would make it be possible to assess the leakage potential of these wells and determine the amount of remediation work required.

For active wells, the only well integrity monitoring information that can be collected at the wellhead is pressure and pressure changes in annuli. Some wells are currently being instrumented with permanent sensors, tracer emitters, and fiber optics; but the challenge is to do this in a way that does not jeopardize well integrity. Transferring data from the well through cables outside the casing is an integrity threat, as cables can constitute leakage paths all along the length of the well. In addition, sensor/cable lifetimes are limited, and at present no long-term well monitoring methods are available to guarantee the safety of wells after abandonment.

Scientific Challenges

For this PRD, the following scientific challenges were identified:

- Effectively determining the current structural and hydraulic states of existing wells is problematic without intervening in wells.
- Extracting useful information from large empirical, heterogeneous data resources for well integrity analysis is a challenge.
- Current remediation materials and methods are inadequate, particularly for abandoned wells.

Research Directions

Enabling remote sensing for field-wide assessment of the location and leakage state of wells

Remote sensing technologies are used for detecting wells and leakage of CO_2, saline formation water, or hydrocarbons at the surface and in the shallow subsurface. Most of these methods rely on proxies for the abandoned wells or the actually leaking fluids. Some of these proxies show considerable natural variation in space and time, so their use requires ground-truthing and establishing a baseline status. As fluids leaking from wells at depth may reach the surface at a considerable distance from well heads, and some depleted hydrocarbon fields include numerous wells, extensive areas may have to be monitored in an efficient way, reinforcing the need for remote sensing.

Current technologies are limited by low spatial resolution (e.g., satellites) or high thresholds for the quantification of concentrations and fluxes in natural environments. New air- land- or water-borne methods should be developed for efficiently surveying larger areas, locating abandoned wells, and defining leakage states by direct monitoring of fluids or proxies near the Earth's surface. Signal processing of multi-parameter attributes and automatic image analysis is needed for fast, objective interpretation of remote sensing information to focus further targeted ground-based investigations to attribute and quantify leakage fluxes.

Discovering low-risk techniques for interrogating the state of wells

Current logging technologies are inadequate to reliably assess well integrity, as they do not provide adequately high-resolution information on defects in and along cement or in nearby rock formations. No methods for assessing the leakage potential or for long-term monitoring of plugged and abandoned wells exist, and such wells are always treated as high risk. Thus, highly drilled reservoirs are less attractive as CO_2 storage sites, despite the wealth of information on the subsurface gathered at these locations. The installation of permanent instrumentation in wells (sensors, tracer emitters, fiber optics) is currently a potential threat to well integrity, as they cannot be installed without jeopardizing the cement seal. The goal of more advanced well integrity monitoring, preferably remote or continuous, gives rise to several fundamental scientific questions:

- Can signals be transmitted along/through well construction materials that allow for detection at the tophole/surface? Which signals should be considered?
- What are the best ways to detect/enhance such signals? Can wells be constructed in a different way to simplify continuous/tophole monitoring or even downhole logging?
- How can signal interpretation be improved to reliably advance from a measurable signal to a full well integrity report? Which signals/responses are correlated to well integrity issues?
- How can permanent instrumentation (sensors, tracer emitters, fiber optics) be installed in wells without jeopardizing well integrity?

Identifying big data analytic approaches capable of assessing large sets of digital well data

A huge wealth of data on well health and how it relates to well construction information, past operational conditions, geologic conditions, and fluid properties exists in well records for the millions of wells that have been drilled in the United States and across the world. Common current practice for assessing wells involves a review of the well records within a field and a ranking of wells in terms of risks based on the most recent downhole well log data, often contained in a spreadsheet or a database. Data mining and machine learning technologies—such as fuzzy logic, pattern recognition, and artificial neural networks—would enable full use of the existing records. Thus, data available from all accessible wells, not just those within a particular well field, could be used to assess well health.

Such technologies have become ubiquitous in several areas of modern society, enabling previously undreamed of applications, such as near-immediate transactions across a worldwide banking system. They have been used in the oil and gas industry to make advancements in a number of areas—for example, to better estimate properties of geological formations in between wells, to predict long-term well behavior, to identify sweet spots in a formation, and to update old well logs to more modern standards (synthetic logs). However, they have not to date been used significantly in assessing well integrity. These approaches are flexible and robust; they can be combined with predictive modeling capabilities and existing data streams. They are able to integrate multiple disparate data streams, as well as the data that will come from noninvasive testing technologies, to provide accurate assessments of well health in real time.

Developing novel remediation and placement technologies

Over many decades, the oil and gas industry has developed a number of methods of remediating operational wells that are no longer zonally isolated. They include the well-established "cement-squeeze" approach, as well as the use of a variety of other materials to seal large to relatively small leakage pathways. It is recognized that existing remediation technology is often inadequate, and that new materials and new methods of determining where and how to apply remediation technology are needed. Another major challenge is to avoid “blind squeeze” by improving techniques for determining where remediation slurries and materials end up and by verifying the sealing ability of barriers in remediated wells.

These methods are useful for active wells, where entry is possible, but not for permanently plugged and abandoned wells that are cut below the surface. These are much more challenging to remediate, and the existing options are both expensive and complex (e.g., drilling relief wells, drilling through plugs, or overcoring). Developing reliable, cost-effective remediation strategies would significantly reduce the risks in CO_2 storage by providing confidence that problem wells can be repaired. It would open heavily drilled reservoirs, where subsurface conditions are well known, for CO_2 storage. The goal is to develop new remediation technologies that can be placed reliably in operational wells, perform in the presence of CO_2, and repair a variety of leakage pathways. The improved remediation technologies should be measurable (i.e., where the remediation material is going) and verifiable (to confirm successful repair). In addition, new technology is needed to safely repair abandoned wells that cannot be easily re-entered and remediated using more conventional methods.

Technology Impacts

The impacts of such technologies would be (1) reduced risks for storage operations; (2) increased options for storage site selection, because sites with preexisting wells could be used; (3) new capabilities for interrogating the status of wells; and (4) cost-effective approaches (relative to risk management strategies) to the remediation of at-risk plugged and abandoned wells.

4.5.9 PRD S-9: Establishing, Demonstrating, and Forecasting Well Integrity

Wells commonly built today in the oil industry are not meant to hold back CO_2 permanently. New developments in materials and embedded sensors can be used to develop future wells that are better suited for long-term CO_2 storage. Once wells are plugged and abandoned at the surface, their underground condition remains obscure. Novel monitoring technologies should enable inspection of well conditions and indicate possible problems before fluids reach near-surface ecosystems. Early warnings facilitate early actions to prevent environmental damage. Next-generation simulation tools will allow reliable predictions of long-term performance of wells and can be used to optimize well completion and monitoring. Next-generation technologies should result in wells that are safe, self-sealing, and self-diagnosing over the long term. These technologies are necessary to minimize cost and effort for long-term monitoring of the large number of wells that will be required for CO_2 storage at the gigatonne scale.

Scientific Challenges

Forecasting the containment performance and sealing ability of wells using current approaches involves a high degree of uncertainty, as predictions are based on very simplistic models. These uncertainties accumulate at the long time scales required for permanent CO_2 storage, leading to low reliability and impeding quantitative statements. To develop new well simulation tools, it is necessary to establish fundamental relationships among parameters affecting well integrity. These tools should be capable of simulating real well conditions, including all the necessary boundary conditions and input parameters—not just simplified models. Laboratory experiments and field investigations of leaking wells can provide characteristic values as input for realistic simulations.

Current well construction practices and materials pose long-term uncertainty with regard to sealing CO_2 in the subsurface. Carbon dioxide and formation water are corrosive to common steel pipes and cements used in well completion. Chemical substances in formation fluids and impurities in CO_2 streams complicate the effects and understanding of corrosion processes. In addition, various forces act on the materials, causing stresses that can weaken the interfaces among rock, cement, and steel; these facilitate further corrosion and access of fluids. These complex physicochemical interactions are not well enough understood for CO_2 storage risk assessment. Self-sealing, as well as self-enhancing corrosion situations, may occur. And it is a scientific challenge to exploit the former for long-term well sealing completions. Current well completion methods do not include or allow provisions for cost-effective, continuous monitoring of well status during well operation and after plugging and abandonment.

Research Directions

Validating processes and fundamental relationships through field and bench-scale laboratory tests

Efforts to improve well integrity are limited by a lack of knowledge of the mechanical and chemical stresses in wells and by the inability to translate existing logging data into accurate images of the annular space, including the distribution of cement and the bonding of cement to interfaces. Current analytical and numerical simulations of well performance emphasize that the results are contingent on assumed stress states in a well. Current logging techniques provide a basis for distinguishing the relative quality of cement but these techniques remain simple qualitative measures of integrity.

Improved knowledge of the subsurface status of wells can be gained by

- Lab and field experiments that measure and evaluate downhole conditions (e.g., mechanical and chemical stress state, changes in stress in response to typical well operations pressure), including lab-scale representations of wellbore systems and the use of downhole logging devices and sensors
- Experiments (lab and field) that elucidate coupled mechanisms in wells and quantify self-sealing or self-opening processes, including fluid flow; mechanical stress; chemical reactions among CO_2, impurities, formation fluids, and well materials; and corrosion of cement-steel systems

- Development and application of field-based measurements of hydrodynamic and material behavior
- Development of accelerated testing standards that predict long-term performance
- Field measurement of flux and leakage leak rates in actual wells
- Permeability characterization of well integrity problems, including damaged annuli and drilling-damaged caprock

Integrating theoretical and experimental approaches to demonstrate long-term performance characteristics

For well operation and reliable prediction of long-term well integrity, high-resolution, high-performance simulations are needed of multiscale coupled thermal, hydrologic, mechanical, and chemical processes within the well and the surrounding porous and fractured rocks. These must accurately describe the transfer of energy and matter among and within the different domains and take into account the different time and length scales associated with these processes. Some chemical reactions, for example, occur at the time scale at which fluids pass through wells; others that alter the rocks in the well surroundings may need decades or millennia to accumulate geotechnically relevant products and effects.

Developing sensor technologies to enable performance monitoring of wells

One approach to improved well monitoring is downscaling of logging devices so that they can be used in slim wells or in the annuli between well strings. New sensor applications may emerge from medical applications, marine technologies, soil science, groundwater sampling, and environmental monitoring. Microsensors for measuring physical and chemical properties, measuring leakage, or monitoring corrosion could be built into robust packages required for logging in harsh environments. Data storage, data transmission, and power supply are challenges for long-term in situ monitoring. Other developments for smart monitoring of wells might include micro-reactors for sampling and lab-on-a-chip analyses, or sensors actively exciting surrounding media. Multiple options for determining mechanical and chemical properties are emerging for fiber optics applications and other devices embedded in cement or included in casings. Wireless, autonomous, or remotely controlled mini-loggers would provide options for inspections in currently inaccessible areas, e.g., of damaged wells. Passive nanosensors could be used as tracers reporting on their passage through the wellbore system.

Developing and qualifying smart materials for well integrity

The use of smart materials has grown across many industries, creating opportunities for a new generation of well-construction materials with purpose-designed properties for well monitoring and remediation. Self-diagnosis or self-monitoring functions are used in piezoelectric ceramics, shape-memory alloys, and optical fibers. Well monitoring can be enhanced by exploiting self-diagnosing materials with tailor-made properties that allow signal detection through tubing. Technologies such as fiber-reinforced plastics with embedded sensors have been used in structural materials for fracture toughness and detection. Optical fibers wrapped along well casings, pressure-sensitive particles, and microsensors embedded in the well cement could be developed, deployed, and tested at relevant subsurface conditions. The addition of contrasting agents, e.g. special fibers, to cement could enhance future well integrity monitoring.

Other smart materials could heal flow paths along fractures within cement and along the interfaces among rock, cement, and casing. Self-sealing materials are already available, e.g., self-healing concrete for subsoil storage of hazardous waste. Microcapsules containing healing agents that rupture upon crack formation could be designed. Existing self-sealing materials could be improved and new ones developed with the properties and longevity required for sealing fractures and micro-cracks. Field tests of novel materials under realistic storage conditions are recommended.

Nonmetallic, compound, and coated pipes reduce corrosion, and nonmetallic pipes facilitate monitoring through well casings. Pipes, made of, for example, fiberglass-reinforced plastics, polyvinyl chloride, or resin-bound plywood, are used for wells in CO_2-rich groundwater. To stand pressures at greater depths, compound materials have been developed for coiled tubing. Coated carbon steel is another option to reduce corrosion and costs for stainless steel. It requires careful installation, though, to avoid damage to the coating. Plastic coatings can be permeable or soluble in supercritical CO_2. Based on such technologies, other nonmetallic pipe materials, compound pipes, and new coating materials—e.g., with nanoparticles or graphene as additives—could be developed. Improved installation procedures could be tested and tailored for wells resistant to impure CO_2, crude oil, acid gases, and brine.

Technology Impacts

Novel technologies will support long-term risk management of wells, lead to improved well construction materials and techniques, enhance understanding of wells' response to CO_2 injection operations, and confirm regulatory assurance for injection and post-injection phases. Other areas of geotechnology and civil construction will benefit from these developments directly by using or adapting geotechnical developments or indirectly by reducing the consumption of limited resources.

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5. Crosscutting Themes

5.1 Crosscutting Panel Report: Crosscutting Themes

In addition to research targeting specific aspects of CCUS, there are a number of emerging themes that crosscut those research areas as enablers. Those also represent PRDs for CCUS. Modeling tools—including multiscale analysis and enhanced use of data analytics and machine learning—can accelerate the development of new materials and the identification and rapid deployment of advantaged, integrated, or intensified process systems. Technoeconomic analysis (TEA), life cycle analysis (LCA), and social systems analysis to select the best options for development are keys to guide CCUS research efforts. But funding and support are needed to improve metrics, benchmarks, and the tools themselves. Research in the fundamentals of CO_2 properties, separation, transport, and reaction is essential for rapid advancement of the science underpinning CCUS opportunities, as is the development of advanced sensors and spectroscopic or other in situ analytical tools for characterization. Integrated or intensified systems that optimize capture together with utilization or storage are also considered under crosscutting themes.

Crosscutting themes and opportunities for advancement of CCUS include the following:

- **Multiscale modeling of CCUS**, using rapid computation software and scale-dependent simulation underpinned by a fundamental understanding of physics and chemistry, to enable robust, resilient, and accurate prediction;
- **Analysis of whole-system CCUS design** using existing and enhanced capabilities and metrics for TEA, LCA, and social systems analysis to address economics, carbon budgets, security of CO_2 storage, and the social dimensions of public acceptability and political economy for current and future scenarios.
- **Monitoring and optimization of CCUS processes and performance** by innovative sensors and analytics to enable the application of big data techniques across the spectrum of component manufacturing, novel materials deployment, capture, utilization, and geological storage, with feedback to optimize and direct real-time, whole-system continuous materials flow.
- **Advanced manufacturing of CCUS components,** including additive manufacturing and 3D printing to reduce capital and operating costs, speed construction, and increase reliability.
- **CCUS process intensification** through the development of advanced materials for separation and conversion, and the use of machine learning and artificial intelligence for the design of integrated ecosystems for capture, utilization, and sequestration.
- **Integration of CO_2 capture (endothermic process) and mineralization (exothermic)**

Whole-systems analysis, TEA, and LCA are key crosscutting tools for guiding and prioritizing research in this field, including expansion to consider the utilization of captured CO_2. CCUS, whether it involves capture and storage, or capture and utilization, inevitably involves the use of integrated systems. Understanding and optimizing process systems is therefore essential. In addition to environmental and economic footprints and impacts, the consideration of risks and incorporation of social aspects of the technology are essential for all CCUS options. The use of assessment and evaluation tools to consider and guide early-stage research for CCUS is one desired area for research funding. Another is to improve the capabilities and reliabilities of the evaluation tools, via improved benchmarking, metrics, and standardization and via improved algorithms and assessment approaches for complex systems.

The emerging disciplines of machine learning and artificial intelligence can be applied to the complex systems analyses of CCUS. For CO_2 capture to make a significant impact in mitigating climate change, the technology must be deployed at a substantial rate. Many systems problems for CCUS span multiple scales: from the atomic or molecular scales; to the mesoscale, at which material structures influence mass transfer and reaction steps; and ultimately to the macroscopic level of integrated commercial processes and industrial parks or ecosystems. Emerging computational capabilities in fit-for-purpose multiscale modeling are important tools for screening materials and concepts for carbon capture and conversion, analyzing complex subsurface flows, and reliably scaling up for deployment. Advanced manufacturing approaches, including additive manufacturing, are needed to accelerate the pace of technological learning and deployment and reduce the costs of producing new capture materials (e.g., sorbents, membranes). Process intensification seeks to examine the integration of capture and utilization; to enable smaller-scale systems with enhanced rates of heat and mass transfer to reduce costs; and to enable distributed modular processes to potentially reduce the need for pipeline infrastructure.

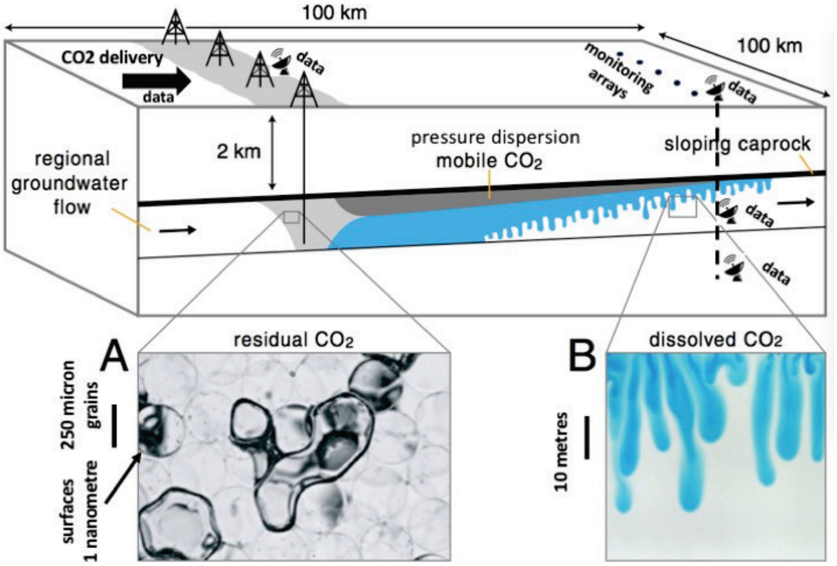
Overall, there is great hope that advanced modeling and computational methods can accelerate the pace of technology development for CCUS. These emerging methods also underpin development across a number of emerging scientific fields. The sidebar “Integration of Surface Infrastructure” presents an example of how multiscale modeling and analysis can accelerate the development of new materials and processes for storage of CO_2.

In addition to modeling and analysis, experimental research in CO_2 thermodynamic properties is needed to generate better models and testing of materials for CO_2 capture or separation and/or catalytic or electrocatalytic conversion to useful products. Sensors for low-cost in situ subsurface CO_2 monitoring and control and for capture and conversion systems can improve CCUS system performance (see the sidebar “Integration of CO_2 Delivery and Storage”), and in situ spectroscopic methods of capture and conversion can accelerate the development of new materials and CCUS processes. Carbon dioxide purification will be important for the emerging field of CO_2 utilization, in which CO_2 is considered a feedstock.

Integration of Surface Infrastructure with Dynamic Management of CO_2 Injection

Scaling up CO_2 injection by 100× from Mt/year to Gt/year requires interactive management of CO_2 injection and storage reservoir performance at low cost [Szulczewski et al. 2012; Haszeldine 2009]. This involves (1) maximizing the utilization of scarce, high-quality geological pore space and (2) ensuring resilient operation during injection and dynamic interaction along a continuous process chain of capture, transport, injection across 10^{12} magnitudes of size for 30–50 years, and then up to 100 years post-injection. Advancing knowledge in this area will require much greater information from the subsurface, which can be gained from arrays of investigations ranging from near-field laboratory experimentation in pore-scale physics, to the far-field creation and installation of subsurface sensor arrays operating remotely over several decades. Combining these analyses requires rapid multiscale modeling focused above, in, and below the reservoir. It will improve prediction of the spatial and temporal effects, mechanically and chemically, of varying pressures rates and temperatures of CO_2 injection.

Integration of CO_2 Delivery and Storage



Top: 3D cartoon of CO_2 transport to an array of injectors across a basin or single reservoir sandstone. Processes at the nanoscale on grain surfaces control the poorly understood petrophysics of CO_2 wetting, contact angle, and pore entry pressure—and hence migration from the micro (millimeters) to the macro (tens of kilometers) scales. Carbon dioxide storage performance is influenced by an interplay of reservoir petrophysics; encasing formation geometry and structure; and pressure diffusion, dissolution, and residual saturation. Near-field effects can be monitored by wellbore metering and sensing. Far-field effects and CO_2 distribution require improvements in sensors and data transmission over several decades during and after injection. Multiscale models can be developed to link the rates, processes, and effects across the 10^{12} sizes and times of operation. | Modified from base diagram in Szulczewski et al. 2012. *Proc. Natl. Acad. Sci.* **109**(14), 5185–5189. Adapted by Stuart Haszeldine, University of Edinburgh

5.1.1 Current Status of Crosscutting Themes

A number of reviews address R&D needs for CO_2 capture and storage: Brown et al. 2016; Alivisatos and Buchanan 2010; de Coninck et al. 2006; NETL 2017; IEA/UNIDO 2011; Dairanieh et al. 2016; Brown et al. 2012; IEA 2013; Ashworth et al. 2015; Mac Dowell et al. 2017; Herzog 2011. Along with basic science needs [Alivisatos and Buchanan 2010], researchers need to address social issues [de Coninck et al. 2006; Ashworth et al. 2015] and improve modeling, analysis tool development, and system studies [Brown et al. 2012; NETL 2017]. Previous rounds of government and industry R&D funding have produced a compound annual growth rate of 46% in patent applications related to carbon capture and storage (or sequestration) between 2006 and 2011 [IEA 2013]. A 2016 Royal Academy of Engineering report illustrated the need for systems analysis in setting priorities, with demonstration and development of storage capability ranked higher than capture research as a priority, for example. It expressed concerns that utilization will be confined to a relatively small impact for the range of applications considered [Brown et al. 2016]. Utilization to date has been dominated by enhanced oil recovery (EOR) but is also addressed in roadmapping studies [Brown et al. 2016; Dairanieh et al. 2016; IEA 2013].

A previous 2010 study [Alivisatos and Buchanan 2010] identified basic crosscutting research needs to support carbon capture and storage (CCS), including the development of improved analysis tools and computational capabilities, development of molecular modeling capabilities for design of new capture and separation materials, improved definition of basic thermodynamic properties for predicting adsorption and membrane transport, and in silico research and discovery for novel materials to reduce costs and improve efficiencies.

The CCSI^2 and Toolset Support Leadership Team [NETL 2017] identified needs for future work in materials characterization, optimal design of experiments, carbon capture device/system modeling, optimization and control, uncertainty quantification, and development of a web-based support community for new and existing users of CCSI Toolset.

A technology roadmap [IEA/UNIDO 2011] study of industry applications underlines the need for improved TEA tools to improve the accuracy of cost evaluations, and performance metrics for evaluating new and emerging concepts relative to base case technologies.

These reviews show gaps between the cost and performance of existing CCS options and the targets for widescale adoption and deployment, demonstrating the necessity of fundamental research in improved capture materials and understanding of storage fundamentals. Utilization, other than known applications in EOR, is less developed; it offers little potential as a significant sink for CO_2 unless new applications for carbon-based products beyond current petrochemical value chains are developed. Opportunities for expanded markets for carbon-derived products include use in concrete (carbonates), direct use of polymeric materials in construction, and use of advanced composites as replacements for steel. As the product of complete hydrocarbon combustion, CO_2 is a thermodynamically degraded carbon for most reactions (other than some mineral carbonations). Many options for CO_2 utilization therefore require reaction of hydrogen with CO_2 to remove oxygen and form, for example, carbon fibers or nanotubes (-C-linkages) or polymeric hydrocarbons ($-CH_x-$). The hydrogen must be derived from renewable or clean energy pathways (with C sequestration) so that net fossil CO_2 emissions do not increase as a result of CO_2 utilization. Systems analysis and life cycle assessment of greenhouse gas (GHG) emissions across the proposed utilization value chain, in contrast to other uses of the renewable or clean energy used to produce hydrogen, is therefore highly important in assessing the value of proposed utilization options.

State-of-the-art LCA/TEA

CCUS is viewed as one of the main pathways of large-scale mitigation of GHG emissions. However, mature CCS concepts are hindered by high costs, lack of policy to value carbon, and lack of public acceptance. These challenges have prompted the development of a much broader set of new pathways that include the potential use of CO_2 to produce fuels, chemicals, and materials. It is important to recognize that all pathways that are consistent with the Paris Agreement commitment require an accelerated transition to net-zero CO_2 emissions and thereafter to net-negative emissions. This implies that any carbon removed from the geosphere must be returned to the geosphere as soon as possible, and additional emissions to the atmosphere must be avoided. Thus, transparent LCA and TEA studies and systems evaluations are of urgent importance, including evaluations of CCUS and of negative emission technologies such as bioenergy with CCS and direct air capture. To optimize R&D investment and resource utilization, a priority is early identification of potential winners—i.e., products, processes, and chains that are (or could be) technically and economically feasible or advantaged, as well as environmentally sound and socially acceptable.

Assessment of the technical and economic characteristics of CCUS technologies is critical for successful implementation and adoption of these technologies. For technologies that are reaching commercialization, the use of technoeconomic approaches and models is already well established [IEA 2017; NETL 2015]. However, at low technology readiness levels (TRLs), these assessments have large uncertainties and varied baselines and are limited for CCUS technologies. The main challenge for TEA is meaningful assessment of very early-stage (TRL 3–4) technologies, as these stages are characterized by an inherently weak knowledge base (because of their early stage of development) and low data availability. Furthermore, for TEAs of new technologies to provide meaningful insights into potential benefits and costs, it is critical that the TEA take into account future developments at the system level. For instance, the increasing share of intermittent renewable energy options (e.g., wind, solar) will change how power plants are operated and therefore the techno-economic performance of CO_2 capture technologies. There are, however, a limited number of TEA studies of early technologies that account for this type of system change [Heuberger et al. 2017].

Early assessment of environmental impacts is also important, as the primary driver of CCUS is the need to mitigate climate change. LCA aims to assess the impacts of technologies and technology portfolios in the environment, for instance, in terms of GHG emissions, water requirements, land-use changes, and biodiversity. LCA takes into account the full life cycle of a technology—it includes the extraction of resources, their transportation, conversion, and utilization; and finally, facility decommissioning and disposal of unwanted residuals. Most LCAs for CCS have focused on the power sector and the impact of deploying (near) commercial CCS technologies. A comparison of 26 LCAs by Corsten et al. [2013] indicates two major knowledge gaps: (1) the focus so far has been on mature concepts (e.g., post-combustion monoethanolamine) while novel CO_2 capture technologies remain understudied; and (2) assessing GHG emissions has been the main goal of most published LCAs. Consequently, there is a lack of understanding of the potential trade-offs between reduced emissions to air and cross-media effects, and of trade-offs among other environmental categories (i.e., water, land-use, terrestrial, air). A similar review was conducted for 16 carbon capture and utilization concepts [Cuéllar-Franca and Azapagic 2015]. The conclusions are similar to those in Corsten et al. [2013]: the focus is on (near) commercial concepts (e.g., fuels) and on GHG emissions. The study also indicates the increasing complexity of carbon capture and utilization concepts, compared, for example, with CCS only.

The scale of CCUS technologies has a significant impact on the environmental footprint (e.g., tonnes of CO_2 captured) or costs of capture and utilization (\$/tonne of CO_2). The scale is also dependent on the feedstocks available for conversion of CO_2 to value-added chemicals. For example, the availability of hydrogen from fossil and renewable sources is critical for some CO_2 utilization pathways. Although several studies assess the amount and economics of hydrogen in different jurisdictions from various sources [Olateju et al. 2014; Collodi et al. 2017], the challenge is that these are seldom integrated with the LCA and TEA pathways. There is an urgent need to integrate these types of research to enable comprehensive evaluation of technology and pathway performance.

The studies discussed illustrate the current use of LCA as a tool to examine the environmental performance of individual chains compared with reference cases (e.g., a power plant with or without CCS, or a product produced from CO_2 vs. the same product produced from fossil fuels). However, the assessment of environmental impacts should go beyond the analysis of individual chains, as it is important to understand the potential environmental impacts of future technology portfolios. This is a new area of development, as exemplified in Hertwich et al. [2015]. That study presents a comprehensive, systematic LCA of the large-scale implementation of climate-mitigation technologies. However, it was conducted for only one mitigation scenario and excluded many indirect effects (e.g., impacts of significant changes to the supply and demand for many products).

Assessments of environmental footprints through LCA, and of the economic viability of new technologies through TEA, are conducted mostly as point estimates, although the data inputs include a lot of variability and uncertainty. The data for the CCUS technologies also suffer from jurisdictional bias. Uncertainty analysis is becoming ubiquitous in the LCA literature. However, it is much harder to handle the increased uncertainty for technologies at low TRLs and with a set of products and routes as expansive as those for CCUS. Some earlier studies consider and estimate the LCA uncertainties for energy pathways, although they are not specific to CCUS pathways [Wang 2015]. Future estimates of LCA and TEA for CCUS pathways should include better and more comprehensive assessment of uncertainties.

Successful development and implementation of CCUS technologies will require the development of integrated evaluation systems that take into account environmental impacts, economics, and social conditions to develop metrics that decision-makers can use for investment decisions and policy formulations. Some past studies have made efforts to integrate in economic and environmental impacts, but these are not comprehensive and that area of study remains an important gap.

Social sciences

Since the 2005 Intergovernmental Panel on Climate Change Special Report on CCS, when there were only a handful of studies available to inform the study, the number of the articles related to CCS and public or stakeholder communications has increased by an order of magnitude, from an average of less than one article per year during 2003–2006 to roughly ten articles during 2013–2016. Ashworth et al. [2015] group research into four main types of assessments: (1) public attitudes and concerns, (2) stakeholder attitudes and concern, (3) communication style and content, and (4) experiences from real-life projects. Each of these areas can be further divided into six areas to account for public and stakeholder concern: deployment cost, deployment scale, perceived risks (to local health and safety), lack of accessible information, need for supporting policies, and adequacy of regulatory frameworks to address the perceived risks. Research is required in all of these areas, as well as in how to integrate insights from social science research with those from systems analysis, based on TEA and LCA.

5.1.2 Scientific Challenges

Specific research challenges are detailed in the PRDs associated with this panel:

1. Integrating Experiments, Simulation, and Machine Learning across Multiple Length Scales to Guide Materials Discovery and Process Development in CCUS
2. Developing Tools to Integrate Life Cycle Technoeconomic, Environmental, and Social Considerations to Guide Technology Portfolio Optimization
3. Incorporating Social Aspects into Decision-Making
4. Addressing Cross-domain Basic Science and Engineering R&D Needs for Intensified Carbon Capture, Purification, Transport, Utilization, and Storage

Modeling tools. Great progress has been made in (1) computational modeling of materials and catalysts; (2) developing modeling algorithms and capabilities to consider complex transport and reaction phenomena at the molecular and atomic scales, and structure-specific transport processes at the mesoscale; and (3) including these processes in larger-scale process system models as needed. Speeding discovery and improving simulation reliability will require improved understanding of the functional response of materials across multiple length scales and in varying environments. This will be achieved via in situ/operando materials characterization experiments and system diagnostics, conducted in concert with theoretical calculations and multiscale simulations. Conventional computational chemistry methods (e.g., molecular dynamics, density functional theory) often are slow in screening through millions of materials to identify optimal materials and material property attributes. Machine learning is an emerging field that greatly expedites the process of materials discovery, including the design of sorbents, membranes, and integrated materials for CO_2 capture and catalytic or electro-catalytic conversion. Catalytic or transport performance for materials in the presence of water and other impurities remains a fundamental research challenge.

TEA, LCA, and systems analysis. Gaps and opportunities for enhanced assessment tools include quantification of uncertainty and methods of application to emerging, low-TRL research opportunities. Transparency in assessments and benchmarking for calibration of base case or current standard performance, including test cases for tool calibration, is needed. CCUS cost calculations often underestimate actual costs, which has hindered acceptance; and incorporating social factors and responses into models is a challenge at the frontier of integrated systems modeling. The ability to address global vs. regional differences is a primary need for model and toolkit development. Comparison studies using existing tools and analysis capabilities are also needed, to set research directions and guide low-TRL research toward desirable target, relative to broader energy system technologies. Addressing all these challenges requires theoretically sound, verifiable data and reliable tools.

Social sciences. For social scientists, CCUS offers the potential for original research into technologies for which most of the public and even many stakeholders have yet to arrive at a considered view. The research base has been growing, but there remains considerable scope for additional basic research into these perceptions. In each of the six areas previously defined (see Section 5.1.1), there has been some noteworthy early research, but there is the opportunity for significantly more research building on actual projects. Additionally, little or no work has been done to incorporate models of social behavior to eliminate or mitigate potential risks posed by social factors. Research in these areas is critical to deepen understanding, improve performance, and drive decision-making functions that will create, for the first time, models and methods that can be used proactively to predict and mitigate social risk.

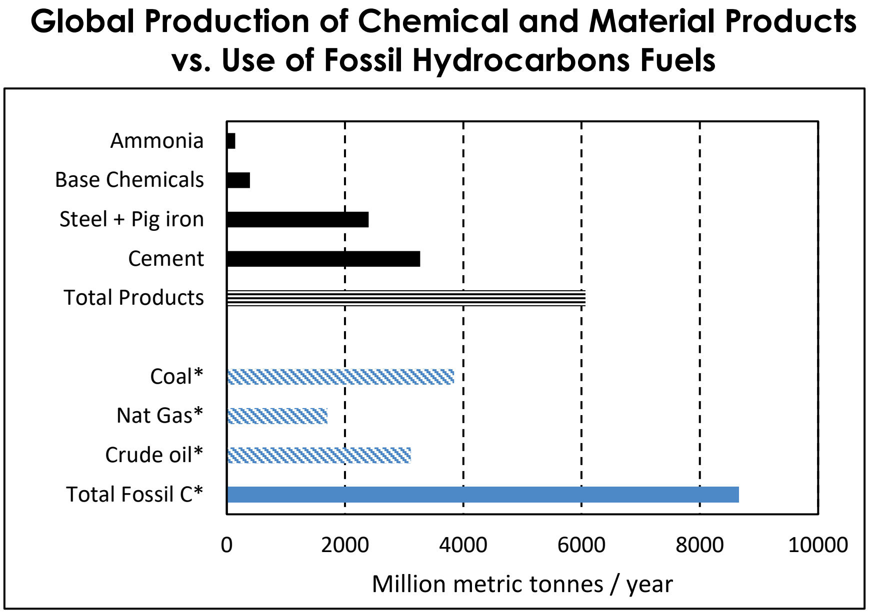
Significant work is required to incorporate social considerations, including social risks, into qualitative and quantitative frameworks and models to guide decision-making. Understanding of the mechanisms by which stakeholder form perceptions, and best approaches for engagement, are needed. For example, the sidebar “The Lacq Pilot Project” in Crosscut PRD 3, illustrating the Lacq project in France, provides an example of integrating technical and social considerations. Such early projects offer opportunities for data collection and learning. At a national and regional level, surveys have been conducted for over a decade, but there are minimal comparative and time-series evaluations of results [Ashworth et al. 2015]. Development of open-source social data sets for scenario testing is needed. Better understanding of societal concerns can help guide research and inform the likelihood of the adoption and ultimate acceptability of different technologies.

Basic science and intensified processes. Research gaps include improved physical properties and thermodynamic models for systems containing CO_2 for use in separations design and transport. New systems are needed for purifying CO_2 (removing NO_x, SO_x, and other impurities) for use as a feedstock. Intensified, integrated processes for capturing CO_2 and converting it to value-added products should be explored, including experimental studies of new materials and reaction systems and preliminary prototype testing. Advanced manufacturing techniques to reduce the costs of membranes, structured catalysts, and other contacting systems can drive down module costs for CCUS components. Process intensification is a strategy to reduce the footprint, volume, and capital cost of process equipment while maintaining performance. It can also involve combining multiple process units into one unit, for example, integrating sequential batch reactions into a single microchannel reactor. Most CCUS processes involve mass transfer, heat transfer, or reaction at an interface, such as CO_2 absorption at a gas/liquid interface or CO_2 reaction on a solid catalyst. Accordingly, process intensification will generally involve increasing the interfacial area in a device or increasing the pressure and/or temperature of the device.

Assessing novel CO_2 utilization pathways and products

Fossil hydrocarbons, derived from crude oil, natural gas, or coal, are mostly used as fuels rather than incorporated into chemical products. The sidebar “Global Production of Chemical and Material Products” shows the global demand for oil, gas, and coal vs. demand for chemical products derived from carbon. Base chemical building blocks include ethylene, propylene, benzene, and methanol but exclude chlorine. On a mass basis, these products represent approximately 9% of crude oil production, or 5% of total oil, gas, and coal demand. This implies that less than 10% of CO_2 emissions could be sequestered in current carbon products, even if the entire chemical industry used CO_2 as a carbon source and used clean or renewable energy to effect the transformation. For carbon use in manufactured products to play a significant role in offsetting fossil hydrocarbon emissions, new, larger-scale markets must be found for carbon products.

New products should be explored for use in construction to enable sequestration at a significant scale. Iron, steel, and concrete are used in the construction industry on a scale similar to fossil hydrocarbon demand. Perhaps 50% of the carbon combusted to produce energy could be incorporated into products if carbon-based materials were used as substitutes for common building materials. The strength and other materials properties of advanced composites are similar to those of steels, and mineral carbonates can augment cement at a potentially significant scale. Building structures currently fabricated from concrete could instead use newly designed polymer/composite blends to enable larger-scale carbon use in products. The higher material costs for carbon-based products could be offset by advanced manufacturing techniques, such as 3D printing of building structures and internal components, and injection-molded buildings fabricated without fasteners at substantially reduced labor costs.



*Tonnes of carbon per year. | Image courtesy of J. B. Powell. Prepared using data from US Energy Information Administration, US Geological Survey, and Andres et al. 2012

Advanced composite manufacturing and 3D printing lead to use of carbon-based composites in place of steel and cements. Top: 3D printed Shelby Cobra Bottom: Injection-molded building structures made from carbon-based polymers and composites. | Image at top courtesy of Oak Ridge National Laboratory. Images at bottom courtesy of Mark Goulthorpe, Massachusetts Institute of Technology

Support for these options will require the development of new advanced manufacturing polymer products—derived from CO_2 or via direct decomposition of methane into carbon products and hydrogen—that meet fire retardance, conductive (graphene), insulative, and other requirements. New architectural designs will be required to support and optimize new fabrication processes. Research directions include catalyst systems and reactor designs for converting CO_2 or methane into thermoplastic polymers (e.g., polyketene) suitable for injection molding and into carbon nanotubes and fibers for advanced composites. The ability to control nanostructure or chemically modify products to impart flame retardance is an important research area.

Systems analyses, including TEA and LCA, are needed to assess the value of these options, given that clean or renewable energy is needed to reduce and transform CO_2 into useful products (except for the formation of some mineral carbonates by spontaneous reaction). There is not agreement on the benefits of pursuing different strategies, for example, substituting renewable energy directly for fossil energy, or transforming CO_2 into value-added products. Liquid fuels are more convenient and are compatible with existing infrastructure, so synthetic liquid “solar fuels” could be made using CO_2 as a carrier for renewable or clean energy, using existing infrastructure and machinery for fuel distribution and use. The value of these options, including the environmental and social impacts, must be compared with the value of direct use of renewable energy.

In addition to enabling basic science and engineering, process pathways and competing options for CCUS—such as use of unabated natural gas and renewable energy resources—should be compared via process systems analysis, TEA, and LCA.

Pathway selection/choices among competing options

The number of products that might potentially be produced from CO_2 is large and increasing. Furthermore, there are numerous pathways—biological, thermochemical, electrochemical, and photochemical conversions; hydrogenation; and solid carbonate formation—by which CO_2 can be converted (Figure 5.1). As the possibilities increase, a priority is early identification of potential winners—i.e., CO_2-based products, processes, and chains that are (or could be) technically and economically feasible and environmentally sound. There is currently a lack of comprehensive assessment methodologies and tools that can be used early-on by technology developers and decision-makers to select and support the development of CO_2 utilization options that would contribute the most to climate mitigation. A comprehensive evaluation of CCUS options should integrate

- The source of CO_2 (biological or industrial process, atmospheric), its characteristics (impurity levels, types of impurities [e.g., water, sulfur, metals], type of capture), and the energy and resource materials requirements
- Source and availability of other feedstocks: H_2, fresh or purified water , noble metals, electricity, heat
- Transformation pathways: biological, thermochemical, electrochemical, and photochemical conversions; hydrogenation; and solid carbonate formation
- Market potential, current and future, and creation of small-scale “stepping-stone” markets and field labs to gain experience and assess business cases
- Desired end-product: fuel, chemical, solid material, polymer; renewable or waste-derived end-product
- Geographical location: feedstock location, local utility prices, distance to end-product market, regulations
- Life cycle impact: renewable vs. waste-based streams, water consumption or withdrawal, end-use, impacts of delayed release of CO_2
- Risks and social consequences and considerations of associated risks and benefits

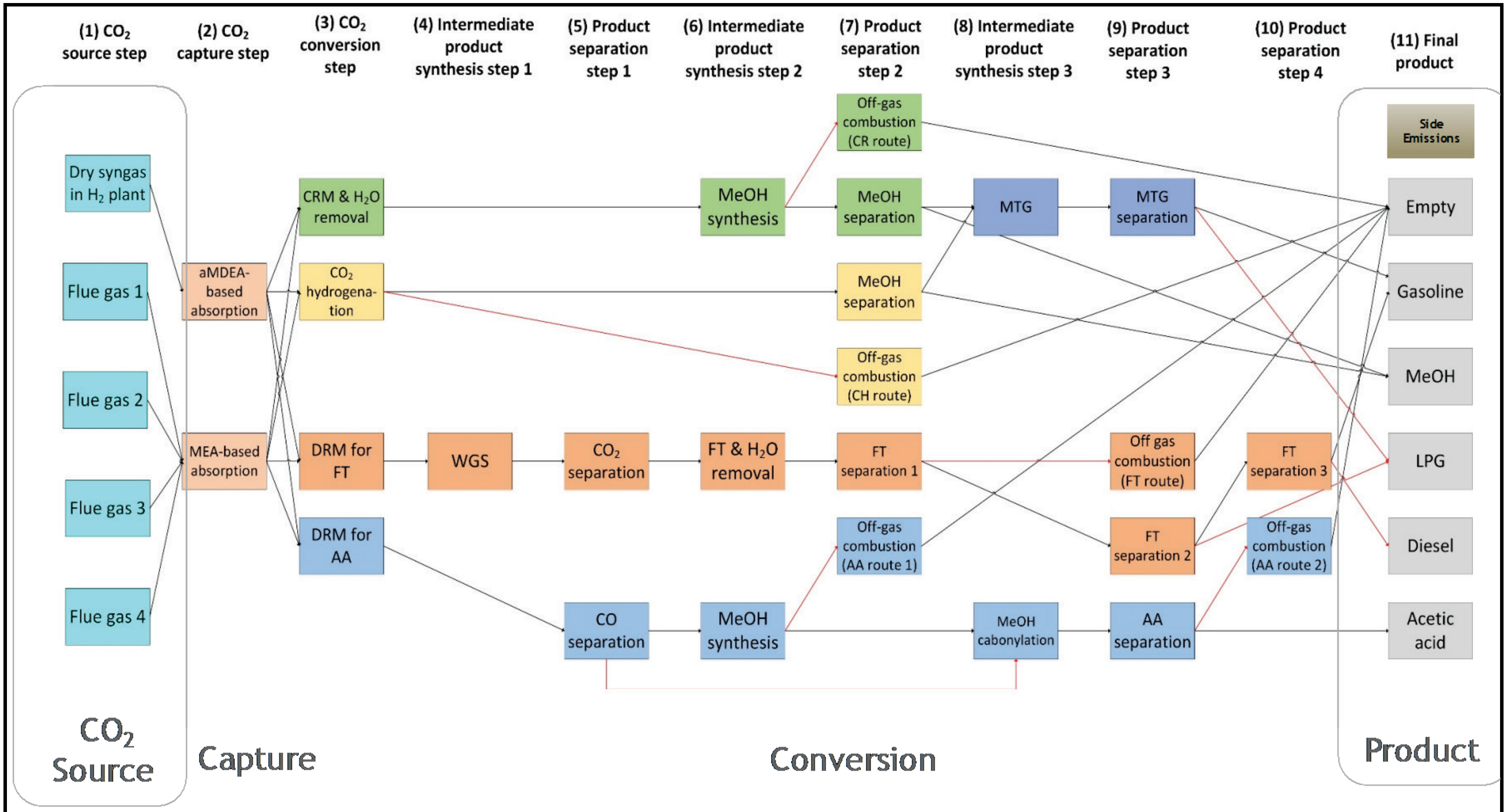


Figure 5.1. If CO_2 is converted to fuel via use of renewable or clean energy, a full LCA is required to assess net carbon and other footprints and the extent of GHG mitigation. If it is converted to chemical products via intermediates such as methanol or acetic acid, a similar LCA is needed to determine the extent and duration of carbon mitigation. | Image courtesy of Jay Lee at Korea Advanced Institute of Science and Technology

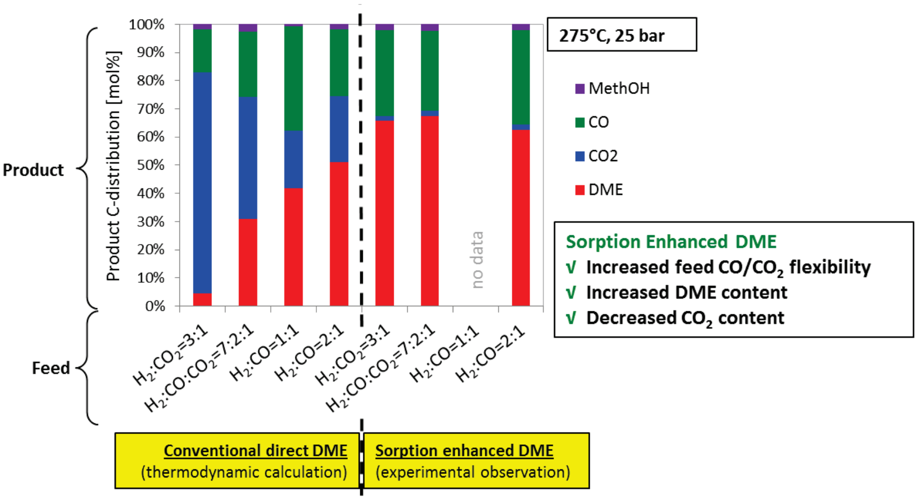
5.1.3 Why Now

Consideration of integrated systems and development of reliable tools for modeling and evaluation of complex CCUS systems is of paramount importance in guiding research and setting goals to make the best use of R&D funding and resources (see the sidebar "Benefits of Integrated and Intensified Processes"). Questions remain regarding, for example, the materiality and potential scale of utilization [Mac Dowell et al. 2017] and the best approach to scaling up CCS technologies [Herzog 2011]. Support for crosscutting areas of research in modeling and analysis will ensure that rapidly expanding capabilities in multiscale modeling, machine learning, and process systems optimization are applied to problems of interest in CCUS. These tools will allow more rapid identification of optimal materials and systems, assist in decreasing risk to enable more rapid deployment, and direct R&D and deployment toward sustainable paths to achieve global large-scale carbon reductions. Development of new lower-cost, more-efficient materials and processes is of paramount importance to future success. The capital costs of CCUS systems remain high but can potentially be reduced via advanced manufacturing approaches. Systems analysis also has the potential to assess not only the costs but also the value of CCUS systems, such as the benefits associated with dispatch and flexibility and the potential for decarbonizing hard-to-reach sectors such as heat- and energy-intensive industries.

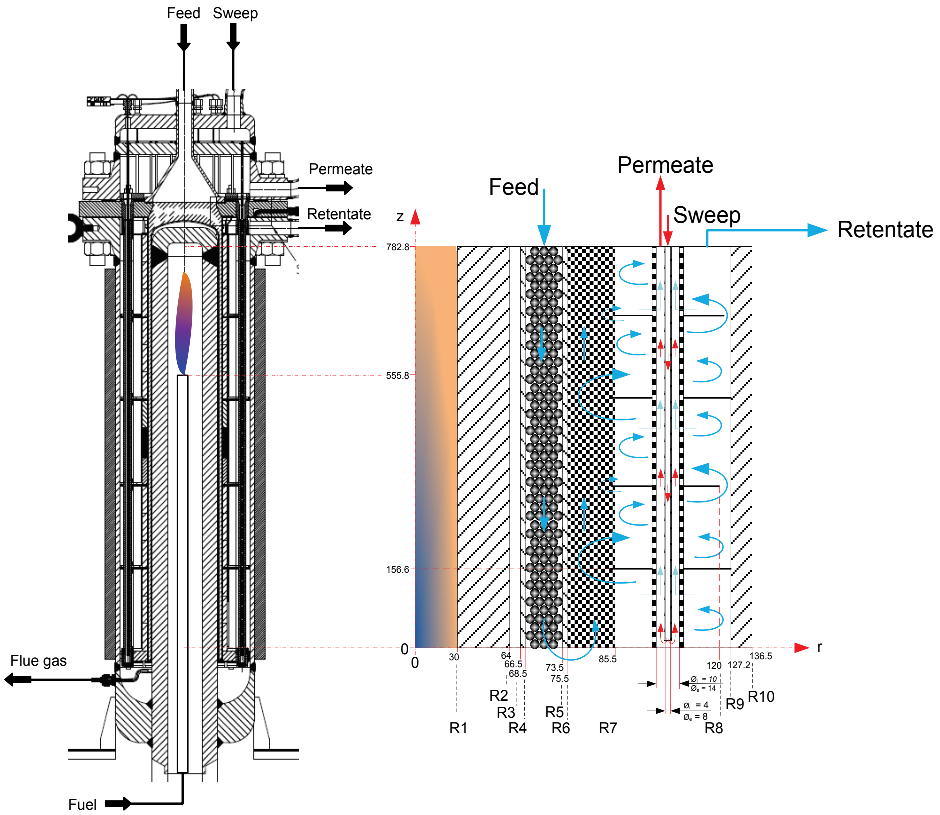
5.1.4 Conclusions

An array of crosscutting research programs in multiscale modeling and analysis—underpinned by basic science and experiments in support of CO_2 capture, storage, and utilization—are proposed to support optimal prioritization of CCUS research opportunities and speed the development and deployment of selected CCUS technologies. These programs take advantage of the rapid pace of new learning and capability expansion in computational analysis, including multiscale modeling, machine learning, and the use of data analytics for developing new materials and exploring complex systems. The proposed programs will provide the metrics and benchmarks needed for effective prioritization of research options. They will rely on recent growth in computational capability to reduce the time and cost needed for deployment.

Benefits of Integrated and Intensified Processes for CO_2 Capture and Conversion



Sorption-enhanced synthesis of dimethylether (DME) from CO_2. | Image courtesy of Jaap Vente, ECN



Advanced reactor design for producing hydrogen with integrated carbon capture options. | Image Courtesy of Jaap Vente, ECN

(Top) The conversion of reactants is often limited by thermodynamic equilibrium; consequently, not all reactants are transformed into the desired chemicals. This is the case when CO_2 and H_2 are reacted to form CO, methanol, and other value-added compounds. One way to overcome these limitations is to remove the steam formed as a byproduct, enabling the reaction to continue beyond chemical equilibrium. The steam can be removed by a sorbent, a water-selective membrane, or simple condensation. The appropriate separation method depends on the allowed steam level. An example is the production of dimethylether from CO_2 and hydrogen. Under standard conditions, the conversion is limited to less than 10%.

However, when a steam sorbent is added, the conversion rate increases to over 60%. After some time, the sorbent becomes saturated and needs to be regenerated. The overall effect is an increased single-pass conversion, less demand on the downstream separation technologies, and smaller recycle streams. This approach requires high-capacity sorbents that can be easily regenerated and catalysts that can operate under transient conditions.

(Bottom) Another intensified process is membrane-enhanced steam reforming with CO_2 capture. The production of pure hydrogen from natural gas includes several catalyzed process steps, including steam reforming and multiple stages of water gas shift. Efficiency can be improved significantly using a steam reforming process with integrated hydrogen removal. A highly selective membrane for hydrogen removal based on dense metal technology is one option. An equally effective reactor is also required, in which the maximum degree of mass transfer, reactive activity, and heat management are combined in an intensified process of reduced module size.

5.2 CO_2 Crosscutting Priority Research Directions

5.2.1 PRD CC-1: Integrating Experiment, Simulation, and Machine Learning across Multiple Length Scales to Guide Materials Discovery and Process Development

Each of the proposed technical research topics proposed for the CCUS themes involves the interactions between different solids and/or liquids with complex mixtures of feedstocks. The underlying thermodynamics and rate controlling processes (transport and kinetics) are likely to be underrepresented in existing databases and in the repertoire of the biologists, chemists, materials scientists, and engineers charged with performing or interpreting the experimental measurements. Moreover, it is certain that large data sets will be constructed to survey the effects of catalysts, materials selection, operating conditions, and time on-stream. Both guiding subsequent experiments and preparing to design scaled-up processes will require addressing common issues in collating, examining, and correlating the experimental results with intrinsic properties of the reactants, products, and catalysts or sorbents. Big-data analytics and machine learning algorithm development should provide means to analyze data to generate insights and knowledge that can dramatically reduce the experimental and simulation efforts required to ensure success at large-scale trials.

Machine learning can accelerate the construction of insightful correlations and serve as a bridge between experiment and theory, and some early successes have been reported. More generally, significant savings in cost and in time can be envisaged from the ability to extrapolate learning across compositions, reaction conditions, and scales of operation. The cost of the proposed crosscutting work would be recouped by avoiding mis-designs, or, worse, failures of scaled-up processes. Of course, the time to start the crosscutting effort is at the beginning of research so that experiments along the way can be arranged to validate existing models and to help differentiate among contending hypotheses.

Scientific Challenges

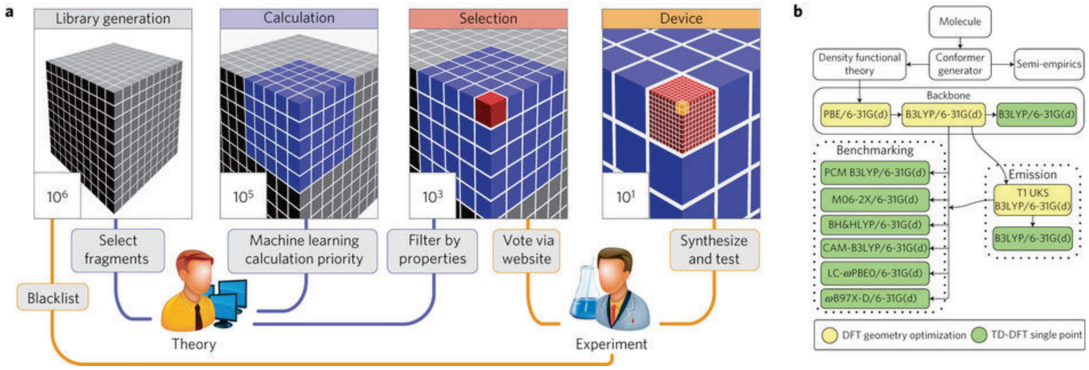
To accelerate the discovery, development, and deployment of functional materials used in specific CCUS technologies, it is critically important that efforts between experimentalists and theoreticians be coordinated to develop in-depth understanding of structure-property-performance relationships across different length and time scales and under relevant and realistic operating conditions. Tight integration among experiment, theory, and simulation is critical to developing accurate, quantitative multiscale models. For example, there is currently a lack of molecular models that accurately and quantitatively describe interfacial processes at varying length and time scales. Those processes are crucial to the electrochemical and photochemical conversion of CO_2, in which photon/electron transfer, mass transfer, and reactions all occur across interfaces.

Moreover, the models developed must be experimentally validated under realistic and evolving operation conditions, so it is necessary to understand the functional response of materials across multiple length scales and varying environments. Thus, there is a need to develop advanced in situ/operando materials characterization experiments and systems diagnostics to be conducted in concert with theoretical calculations and multiscale simulations.

Conventional computational chemistry methods (e.g., molecular dynamics, density functional theory) often are slow in screening through millions of materials to identify optimal materials and material property attributes. Machine learning can expedite this process: the properties of a few materials (a training set) can be computed and the information used to identify the optimal materials from a larger set without explicitly conducting simulations of millions of materials [Gómez-Bombarelli et al. 2016]. In the carbon capture arena, machine learning algorithms have been applied to selecting high-performing metal organic framework materials for CO_2 capture [Fernandez et al. 2014]. Other work includes the formulation of a novel solvent for capturing CO_2 [Cantu et al. 2016] and the specification of a novel sorbent whose performance for capturing CO_2 improves in the presence of water.

Designing Molecules via Computational Screening and Synthesis

In Gómez-Bombarelli et al. [2016], from a chemical space of 1.6 million molecules, novel organic light-emitting diode molecules were identified using a combination of machine learning algorithms and density functional theory simulations. The research team combined this approach with experimental synthesis to find molecules with quantum efficiencies as large as 22%. A machine learning algorithm was used as another level to screen/filter the candidates to save computational time. This information was then used to effectively guide experimental synthesis efforts.



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These are inspiring efforts but, in most cases, the materials themselves come from known databases. Artificial intelligence (AI) / machine learning methods are needed that can create and/or design completely new materials. Moreover, handling the vast amounts of data flowing into large libraries used for training purposes and screening is inherently a "big data" problem; therefore, big data analytic methods will need to be developed and applied. As the size scale of the data increases, it will be necessary to use high- performance computing to optimize machine learning algorithms and perform computation-intensive calculations.

Research Directions

Currently, the gap between experimental and theoretical efforts stands as a key barrier to rapid, efficient materials screening/process development.

Develop novel experimental methods using in situ/operando sensing

To better establish structure-property-performance relationships, it is important to develop novel experimental methods that determine the physiochemical properties of materials under not only static but also dynamic conditions. Novel in situ/operando sensing techniques need to be incorporated into experimental efforts. They need to cover broad length and time scales from atomistic and molecular interactions at fluid/solid/gas interfaces. Such in situ/operando experimental methodologies may use electrons, ions, x-rays, or neutrons to track the structural and chemical changes when materials are subjected to realistic environmental conditions (e.g., temperature, pressure, gas/fluid composition). For example, sorbent materials, membranes, and catalysts will be subjected to a variety of flue gas conditions and purity requirements in real applications.

Develop "big data" analytics and machine learning methods to analyze/mine data from experiments and simulations

Significant advancement in scientific instruments and analytical techniques allows for the interrogation of material from atomic to mesoscopic length scales via multimodal signal acquisition. When these techniques are integrated with in situ/operando experimental experiments with time-resolved measurements, a significant number of multi-dimensional datasets will be generated. The bottleneck then becomes how to transfer, store, and analyze these large-volume data sets. Moreover, to analyze these data sets along with other relevant experimental and simulation data, new data analytic algorithms must be developed using high- performance computers available through programs like HPC4 Manufacturing [Lingerfelt et al. 2016].

Develop and use AI methods for materials discovery

AI and machine learning will be integral aides in rapidly screening candidate materials by data-mining specific physiochemical property attributes. Existing and big data analytics and machine learning methods need to be tailored and new ones developed to enable analysis and mining of data from experiments and simulations using high-performance computing. The materials used in the machine learning applications so far have come from known databases. AI/machine learning methods are needed that can create/ and/or design completely new materials.

Technology Impacts

Research efforts in the outlined directions should enable more predictive designs of materials, which will accelerate the pace of discovery of functional materials (e.g., catalysts, membranes, sorbents, structural materials, and biocatalysts) that are cost-effective, durable, and scalable and perform effectively in large-scale applications. Such research efforts should enhance the fundamental understanding of interfacial chemical reactions and kinetics, which is the fundamental underpinning of the rational design of new materials or modification of existing materials. Integrated efforts to develop experimentally validated, interpretable, and quantitative models will increase the viability of large-scale tests or real applications and are expected to bring 2–5× improvements in productivity and increased return on investment. They should also provide a framework for multidisciplinary, global scientific interaction.

Conclusions

CCUS research is scientifically challenged by the phenomena and decisions occurring over a wide range of length scales, from molecular to process to global enterprise. Currently, the pace of innovation is retarded by the lack of coordination and cooperation between modelers and experimentalists across scales. Currently, very few experimentalists use modeling and simulation tools in their materials and process development efforts, as ‘“novice-friendly’” software tools are lacking. This PRD will attempt to tie experiment with modeling across germane length scales to accelerate discovery and innovation by taking advantage of new advanced computing, AI, and in situ/operando characterization tools. The impact will be large and far-reaching, accelerating discovery and innovation, saving wasted effort and investment, increasing the viability of large-scale trials, and paving the way for a new framework for multidisciplinary collaboration.

5.2.2 PRD CC-2: Coupling Basic Science and Engineering for Intensified Carbon Capture, Purification, Transport, Utilization, and Storage Processes

Basic science and engineering needs for CCUS span a wide range of topics, including thermodynamics for CO_2 and its common impurities, purification of CO_2 for the newly emerging subject of CO_2 use and for transport and storage, and intensified and/or modular process concepts to address the need to reduce the capital costs of technology deployment. Development of improved sensors for monitoring and in situ tools for examination of interfacial and subsurface phenomena are also important as enablers of enhanced experimental capabilities and of systems optimization and control in deployment. Studies in this space can be experimentally based and augmented by the multiscale or system modeling tools also described under crosscut capabilities.

Goals for fundamental work in thermodynamics include

- Development of a new molecular-based thermodynamic approach for the reliable description of fluid throughout the fluid phase diagram
- Explicit treatment of allowed reactions within this new framework to describe potential cascades of reactions within the CO_2 mixtures in the transport and storage value chain
- Efficient coupling of this framework with a computational fluid dynamics framework
- Curation of a database of high-quality experimental data against which to test and refine the modeling approaches developed

Goals for process intensification target a substantial decrease in capital and operating expense and the use of modular conversion processes, which can save pipeline transport costs. Additive manufacturing (AM) goals seek to speed the rate of discovery as well as the design and manufacturing of advantaged materials for CO_2 capture, conversion, separation, and purification.

Scientific Challenges

CCUS requires the compression and transport of mixtures of CO_2 (+others) from approximately ambient conditions to supercritical conditions. There is currently no single **thermodynamic framework** suitable for consistently describing the entire fluid range—existing theories require modification to describe the critical region, e.g., crossover treatments. The following are specific challenges:

- Develop a new framework for the unified description of the entire fluid phase diagram. Specific challenges—beyond vapor-liquid equilibrium thermophysics: surface tension, viscosity, triple point, sublimation, solid-fluid transitions, corrosion phenomena, failure modes (brittle/ductile fracture).
- Efficiently couple a predictive thermodynamic framework with a reliable computational fluid dynamics package to describe the behavior within the pipeline and injection wellhead.

The radical capabilities of AM, including 3D printing, create a new frontier for scientific and technical endeavors. Already, researchers in CCUS are using AM to functionalize materials, create new reactors, and even design experiments to assess fluid-pressure feedbacks in fracture networks. Going forward, a few areas suggest rapid progress and high impact in CCUS:

- Intensified adsorbers/reactors: Researchers have already created fit-for-purpose devices that separate and do chemical work in one step (see Figure 5.2, for example). This is accomplished by incorporating nano- and micro-chemicals (including carbon nanotubes, catalysts, enzymes, and even living microbes) into printable inks, which can be fashioned into permeable membranes. These added materials execute conversion for exothermic reactions readily and can be augmented by thermal, electrical, or photic input to execute endothermic conversions. This is a pathway to functionalizing metal-organic frameworks, electrocatalysts, and more—the potential applications for CO_2 conversion and CO_2 capture are only now being explored, and they appear limitless.

- Improved-stability membranes, catalysts, and electrocatalysts operable at higher temperatures and with economically viable stabilities and fluxes/activity remain a material and systems challenge for integrated capture and conversion of CO_2.
- Ink and alloy design and modification: Adding components to printable inks and alloys is only one way to design and functionalize new materials. It is possible to design new inks from scratch, with specific properties (like permeance) that can be designed. In addition, microscale and nanoscale interleaving of existing materials provides new properties not found in nature, such as ultra-lightweight alloys, zero-thermal-expansion materials, and tuned thermoelectric response. These approaches can be valuable in producing lower-cost materials, sensors for monitoring, and membranes or catalysts for capture and conversion.
- Synthetic rocks: High-fidelity synthetic models of rocks, including accurate and precise pore structures, fracture networks, and chemical properties can be made via AM. Helpfully, they can be made transparent to light, neutrons, electromagnetic fields, and other nondestructive interrogation techniques. Such synthetic rocks can help resolve fundamental issues of CO_2 transport in multi-phase porous media, including the role of fracture dilation in transport, how wettability angles change dynamically, and the geometric effects of mineral precipitation and dissolution.

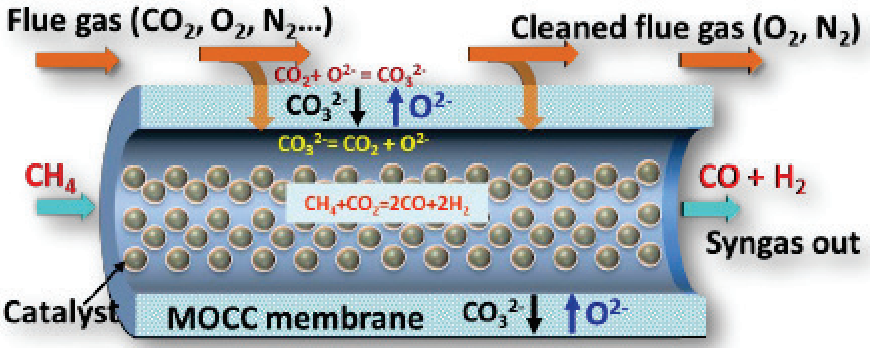


Figure 5.2. Process intensification: Mixed oxide- and carbonate-conducting (MOCC) membrane reactor for heat- and mass-integrated capture of CO_2 from flue gas for direct use in syngas formation from natural gas. | Image courtesy of K. Huang, University of South Carolina

Because of the rapid advance and evolution in this space, there are abundant opportunities for participation by countries, companies, universities, and research laboratories, which can begin to invest in facilities and groups to explore and expand AM work. Coordination, nationally and internationally, among research groups to share learning is an urgent and low-cost undertaking for the research and development community.

Improved understanding of interfaces (fluid–fluid, fluid–solid, gas–solid) though improved characterization, modeling, and development of new spectroscopic tools can be used to improve the efficiency of transport and reaction steps involved in carbon capture and sequestration.

In-silico design approaches using the modeling tools described in the crosscut technologies panel report should augment the direct experimental and physical research and exploration of integrated, advanced concepts in carbon capture and utilization.

Technology Impacts

The technology impacts from basic research and development studies in complex phenomena underpinning CCUS include these:

- Improved accuracy and reliability of CO_2 flow, transport, and separation via improved thermodynamic data and models.
- Capital cost reduction via developing novel systems for purification and intensified processes combining or integrating (Figure 5.3) capture and conversion steps for utilization, along with enabling modular processing to avoid pipeline costs while co-producing value-added products.
- Advanced manufacturing methods to reduce capital cost and improve performance in modular intensified process equipment, as well as novel membrane, adsorbent, electro-catalyst, and catalyst materials used for both conversion and purification of CO_2.
- Improved sensors for monitoring of CO_2 emissions, transport and sequestration; improved in situ analytical methods for characterizing membrane, adsorbent, and catalytic materials leading to more rapid identification of high-performance systems.

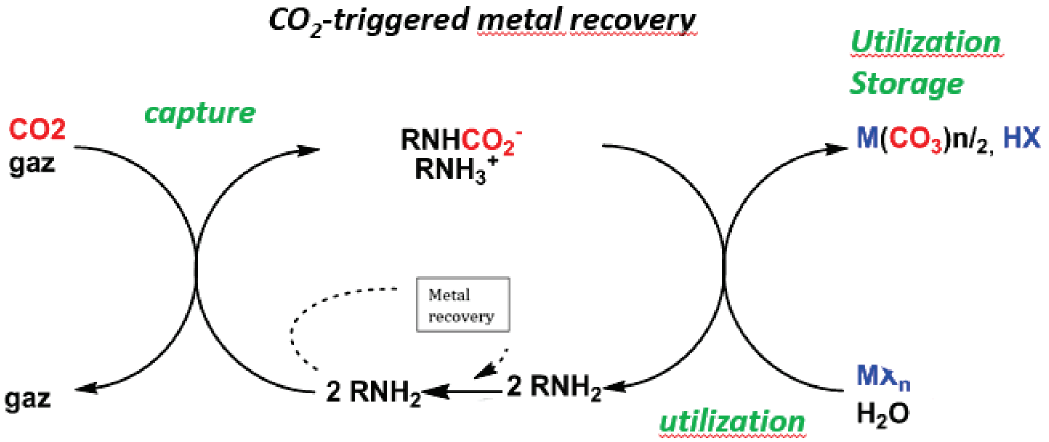


Figure 5.3. Process-integrated CO_2 capture with cyclic use for mineral carbonation and metals recovery. Poisson et al. 2016. | Image courtesy of LeClaire Julien, University of Lyon, France

Conclusions

Crosscutting research entailing experiment combined with theory to improve fundamental understanding and modeling of CO_2 properties, and design of materials and systems for intensified separation and conversion to value-added products in integrated systems, can lead to a step change reduction in CO_2 capture, transport, conversion, and/or storage costs and increased opportunities for CO_2 valorization.

5.2.3 PRD CC-3: Incorporating Social Aspects into Decision-Making

Trust, knowledge, awareness, and risk perception all should be investigated using both experiments and real-world evidence to ascertain the effects of public and stakeholder communication and engagement. New research, lessons learned, and best practices for stakeholder engagement continue to emerge from CCUS experiences; but to date, they have been insufficient to reduce risk and uncertainty in project design and development. New studies are critical to deepen the understanding of social factors and how they can be integrated in models to facilitate decision-making. Consideration of and research in stakeholder engagement, social influencers, decision-making factors, response to technologies, and changes associated with CCUS over time are all needed to gain insight and perform critical engagement activities needed to move CCUS from public to private industry. Effective stakeholder engagement fosters relationships among project developers, regulators, and communities. Thus, it is critical to establish open lines of communication and address stakeholder questions and concerns while identifying and mitigating potential risks. Research can help to build qualitative and quantitative models, which in turn inform decision-making and facilitate innovative approaches to CCUS and stakeholder action by reducing risk, decreasing barriers to understanding, and accommodating changing societal factors and systems.

Scientific Challenges

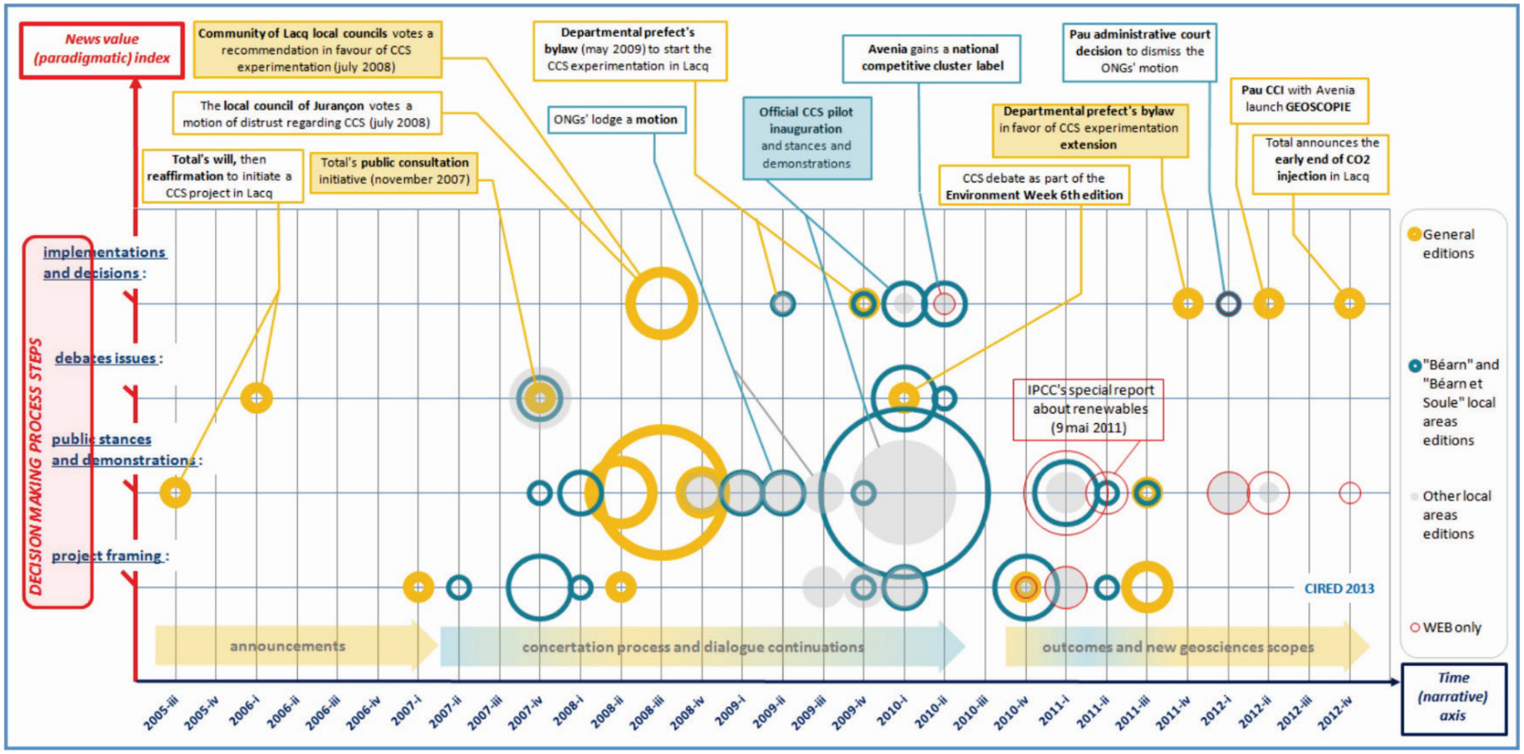
The roots and consequences of social factors have significant impacts on CCUS development and deployment. The continued high degree of uncertainty and risk centering around social aspects of CCUS are often poorly incorporated into considerations throughout the value chain, deployment projections, and tensions between societal and technological drivers. For example, the sidebar “The Lacq Pilot Project” delineates social impacts vs. timeline for Total’s pilot program in carbon capture and storage.

Stakeholder engagement is one way to address this challenge. It is widely recognized as a critical component of successful CCUS projects. Indeed, lack of stakeholder engagement, public awareness, and public support are often cited as major barriers to the development and implementation of CCUS projects and of associated technologies. At present, many CCUS demonstration projects are conducted through partnerships among government, industry, nongovernmental organizations, and academia. Demonstration projects and commercial projects coming online have multiple stakeholder groups, including the general public, educators, government, regulators, industry, landowners, farmers, and others, depending on specific circumstances. Stakeholders may have varying interests, information needs, and concerns that need to be acknowledged and addressed. Furthermore, stakeholder attitudes and levels of action are highly variable and can be affected by related or unrelated events.

Another aspect of this challenge is the incorporation of social considerations into qualitative and quantitative frameworks and models to guide decision-making. Although there is an understanding of the importance of stakeholder engagement for eliciting information, concerns, and preferences, and for working with these stakeholders as partners, there has been little work to integrate the results of these studies into predictive models or anticipatory strategies to address risks associated with social factors. Social interactions, knowledge, perceptions, and attitudes among stakeholders are in a constant state of flux between each entity’s own experiences and the experiences of other entities. These are fed into the approaches that are used for decision support in real time. For example, the responses of individuals and groups to a seismic event or a leak (whether perceived or real) may coalesce into opposition to the project that could influence the project outcome. These responses could also grow into mobilizations that impede the overall roll-out of CCUS.

The Lacq Pilot Project

The Lacq Pilot project is a fully integrated carbon capture and storage project operated by Total in the Lacq region of southeastern France. From 2009 to 2013, the project captured more than 51,000 tonnes of CO_2 through oxyfuel combustion at a gas-fired power station, transported it by pipeline, and injected it safely into the nearby Rousse geological reservoir.



Stakeholder engagement and social impact management for Total Lacq Pilot. | From *The Lacq Pilot*. Copyright by Total Exploration and Production. Image courtesy of Total.

It is essential to understand and consider how opinions are formed, how they are spread through social networks, how these cascades may coalesce into mobilizations that enable or impede the deployment of technology—and how these dynamics can be affected by proactive and ongoing stakeholder engagement. Therefore, these characteristics must be integrated into the methods and models that are used to guide decision-making. Frameworks and models such as these are widely used to evaluate the costs, potentials, and trajectories for the ultimate deployment of technologies like CCUS and their potential to address the environmental conditions they are designed to address. By definition, representations of these technologies and their interactions within energy, environmental, and economic systems are stylized, and "an improved representation of human behavior is at the frontier of research for [Integrated Assessment Models]" [McCollum et al. 2017].

Another critical component of stakeholder engagement is the potential for risk reduction and mitigation through effective processes. The integration of dedicated stakeholder engagement strategies can help reduce project risks and risks associated with public concern. Through the risk assessment process, project managers gain insight into potential project risks and can develop risk mitigation strategies and stakeholder engagement for communicating about potential risks. This approach has proved effective for multiple CCUS projects, such as the Illinois Basin–Decatur Project, Quest, Otway, and Boundary Dam. However, additional research is needed to define generalizable methods for success that can be applied more broadly as projects move toward commercialization and wide-scale deployment.

Research Directions

Improve understanding of behavioral decision-making, information cascades, social networks, stakeholder participation, social mobilizations, tipping points, and social dynamics to mitigate risks in how social factors influence innovation, infrastructure, technology development, and diffusion dynamics.

Social networks and communication strategies change frequently, and emerging social media can quickly alter the landscape of how information travels. To better inform decision-making and address risks, it is critical to understand how mobilization occurs, what tipping points can generate responses, and how these factors change with larger deployments of CCUS.

Study stakeholder social dynamics of projects, risk factors, and changing environmental conditions using social science methodologies to predict and mitigate social risks through both quantitative and qualitative models.

As an example of risks, induced seismic activity has the potential to alter social response to regional storage complexes. Using models that characterize and predict social mobilization mechanisms can help define risk mitigation strategies.

Understand the mechanisms by which stakeholders form their perspectives, how these perspectives are influenced by different forms of engagement, and by which stakeholders revise their opinions because of new, different, or potentially contradictory information.

As increased awareness and knowledge about CCUS activities is formed, it is critical to have effective stakeholder engagement. Research in this area allows for the real-time development of tools and methods that proactively address changing social environments and responses to emerging developments in CCUS.

Develop methodologies, such as social site characterization, that generate longitudinal data sets that can be used to understand long-term impacts of social factors on deployment of CCUS technologies, feed into model assessments, and decrease barriers to deployment.

At the local and the national level, there has been virtually no effort to properly track attitudes over time. Creating mechanisms to track and understand long-term attitude components, changes, and demographics are key to decision-making and project implementation. The development of open-source social data sets that can facilitate understanding from multiple perspectives will decrease uncertainty and drive innovation in social engagement. Longitudinal attitudinal tracking through surveys is one component of social site characterization that has potential in areas where projects are proposed or operating. Ascertaining a baseline understanding of what the public knows and issues about which people share concerns or questions can be a useful first step in engaging with a local host community. Longer-term monitoring of opinions over time will also provide valuable feedback on how a community views a project and its ongoing development.

Technology Impacts

Increased understanding of and improved access to data surrounding social impacts on CCUS technology deployment will provide mechanisms to address risk communications, facilitate lab and field deployment, and proceed down the learning curve to higher technology readiness levels. Breakthrough social science research and stakeholder engagement approaches that generate consensus around CCUS technologies will drive commercial projects and reduce risk factors that inhibit the wide-scale deployment of CCUS. Driving down uncertainty in social factors, increasing understanding of the impacts of social risk, and improving modeling capabilities reduce significant barriers while providing supportive data for creating and implementing successful engagement strategies.

Conclusions

Stakeholders can find it difficult to compare risks in the abstract associated with a technical subject such as CCUS, except perhaps in regions where there is already extensive oil and gas production. Existing studies have demonstrated that context matters, and that where legacy issues abound, projects are likely to meet increased opposition. The value of assessing experiences from real-life projects is the contribution they make to understanding factors that may affect attitudes toward CCUS, in terms of both success and failure, and that may not be revealed in experimental settings. Moving beyond understanding basic social factors and obvious impacts is necessary to decrease social risks, improve program and project performance, and develop qualitative and quantitative mechanisms for predicting and/or mitigating social barriers.

Although there has been significant improvement in monitoring and modeling techniques for CCUS that could be used to demonstrate the environmental integrity of storage projects, the social risks and the inability to mitigate for social impacts remains critical in CCUS deployment and decision-making. Social science needs to continue to be used to understand and drive new innovations in stakeholder engagement, networks, communication strategies, and activism. Furthermore, these insights need to be integrated with TEA and LCA to generate comprehensive evaluation of CCUS technologies and systems.

5.2.4 PRD CC-4: Developing Tools to Integrate Life Cycle Technoeconomic, Environmental, and Social Considerations to Guide Technology Portfolio Optimization

Implementing CCUS technology solutions requires optimization of plant and project performance and economics, life cycle–based environmental stewardship, market interaction, and resource management. A coordinated international commitment to enable step-change progress toward ultimate carbon reduction goals is challenged by insufficient and sometimes inaccurate data, inconsistent modeling assumptions, and incomplete metrics. Further development of global CCUS community evaluation systems, with guidelines for practice, is needed to effectively and efficiently communicate technology and research direction. Data availability and representation challenges hinder the proper characterization of existing operations and CCUS technology performance. Real-world variability in national resources, market conditions, and value propositions further challenge coordinated research. *Research to create a consistent evaluation system and develop the data resources to uniformly guide research and technology evaluation is a priority to enable the examination of systematic and crosscutting issues for CCUS technologies*. Outcomes of this crosscut research, conducted using high-quality, consistent practices, will enable coordinated international and national technology improvement and inform investment priorities with confidence. A globally consistent evaluation system will support robust technology screening to enable early-stage prioritization of technologies and specific R&D targets and activities, support stakeholder and public interaction for technology acceptance, and improve data gathering and analysis and technology evaluation to maximize CCUS investments nationally and globally.

Scientific Challenges

The number and complexity of novel CCUS technologies, including the future need for negative emissions, are increasing; and their impacts across multiple environmental categories and upon resource availability, material flows, and market potential are yet to be quantified. Specifically, concepts and technologies related to advanced carbon capture (e.g., sorbents, new solvents) and the entire field of CO_2 utilization (including a multitude of conversion pathways, materials, and final products) have raised important new research questions that demand more focused and responsive system-level tools.

Studies to date have focused on economics and GHG emissions, but a much broader set of impacts and trade-offs will drive acceptance of these technologies—including water, land, air quality, and biodiversity. Resource availability issues, such as the large-scale supply of energy and hydrogen feedstocks for CO_2 utilization, are critical to assess and are not considered in typical system assessments (see the sidebar “Need for Scalable Feedstocks”). For example, production of hydrogen from renewable sources often suffers from resource constraints.

Current system tools are designed for application to nearly commercialized technologies with well-characterized systems. Even so, most studies of technologies at high TRLs conduct only a basic uncertainty assessment, if any. Many studies report impacts using point estimates. When low-TRL concepts are being developed, there are much higher levels of uncertainty and a weak knowledge base. Most evaluations are point estimates based on first-principles calculations or preliminary experiments. Assessment of these concepts requires more focused effort on representing and incorporating uncertainties in the evaluation to inform important decisions as the concept evolves across the early TRL stages.

Another challenge in evaluating and comparing CCUS concepts and technologies is a general lack of transparency due to the proprietary status of much of the data and the strategic nature of the field. Tools and methods also tend not to be shared widely, leading to challenges associated with accessibility, comparability, and reproducibility in data, tools, and methods. International consistency is important to encourage efficiency and effective allocation of resources and avoid duplication.

Developing a full set of performance metrics is essential to set priorities for research directions. To determine these metrics consistently and comprehensively requires integrating insights derived from a broad set of tools and expertise, including LCA, TEA, resource availability, and market potential evaluation. Integrating these insights is difficult because of issues such as disparities in methodological assumptions around boundaries, geographic and temporal scales, metrics, and different expertise of the experts engaged in the analysis. Transparency in assumption and methodology will be essential for effective systems tool development.

Research Directions

Develop analytic techniques working with limited amount of data and large uncertainties. A major challenge for system evaluation of early-stage technologies (TRL 3 and below) is a lack of operational data from facilities and demonstrations. Data for system evaluation, especially LCA and TEA, are needed and are often generated from theoretical calculations or engineering simulations. Such data are often speculative and subject to great uncertainties. Analytic techniques and guidelines need to be developed so that data generation will follow scientific, consistent protocols. The protocols will also need to address uncertainties in early-stage technology development.

Need for Scalable Feedstocks for CCUS Development

Much current CCUS research tends to assume as a prerequisite an abundance of free or very cheap, low-carbon hydrogen and electricity, precious metals, and other inputs. Furthermore, high-purity feedstock streams are often assumed, disregarding the impact of impurities on each CCUS pathway.

Any technology that relies on over-optimistic assumptions is prone to failing as it nears commercialization, after consuming much time and money. Given the urgency of CCUS for climate change mitigation, avoiding late-stage technology failure is crucial.

Robust resource assessments for novel technologies should be developed and integrated in early-stage evaluation tools. Specifically, technoeconomic assessments of hydrogen production should be integrated in utilization pathway evaluations. Design flexibility due to feedstock variability should be taken into account by researchers, including CO_2 impurities and renewable energy intermittency and storage. Such efforts are likely to accelerate the necessary synergy between CCUS and renewable energy.

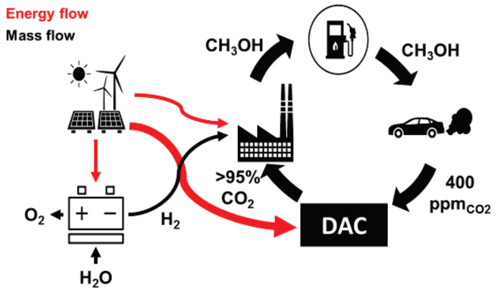


Image courtesy of Niall MacDowell, Imperial College, London

Establish a set of standardized evaluation metrics. The evaluation system will need to be comprehensive, including environmental, economic, and social metrics for CCUS technologies and benchmark technologies. Environmental metrics should include multimedia environmental issues (such as emissions and discharges to air, water, and land), ecological effects (e.g., biodiversity), and resource depletion issues. Economic metrics should include both private and societal costs and benefits, capital investment requirements, and so on. Social metrics will include environmental justice, social acceptability, and legal compliance. Standardization of metrics for plant economics is also essential. While environmental and economic metrics can be quantitative with models and simulations, some of the social metrics may be qualitative. Research is needed in how to integrate these metrics and how to transparently communicate the results to stakeholders.

Develop methodologies for integration of evaluation metrics. There is a need to develop methodologies that can be used internationally to integrate the environmental, economic, ecological, resource depletion, and social issues. Doing so would help investors and decision makers in different jurisdictions make decisions with regard to identifying promising CCUS pathways.

Develop tool kits specific to CCUS technologies and with regional fidelity. Based on the preceding two steps, modeling/simulating tool kits could be developed for CCUS technology pathways that address analytic issues specific to CCUS technologies (Figure 5.4). Such issues include carbon sinks and sources, the energetics of key stages of CCUS pathways, and environmental hot-spots. These tool kits could be developed with existing tools in the energy and environmental fields and through interaction with CCUS technology developers. They will need to be accessible to technology developers and stakeholders, such as non-governmental organizations, for identification of R&D opportunities and transparency. The tool kits also should be sufficiently flexible to address global regional differences in developing and deploying CCUS technologies and carbon-neutral/carbon-negative pathways.

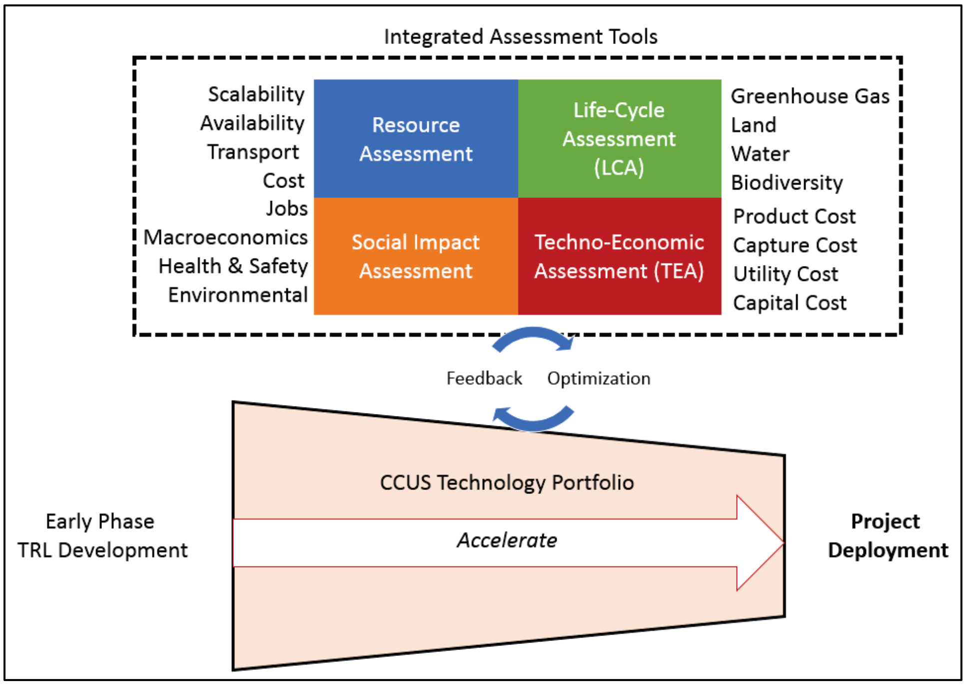


Figure 5.4 Tool kit overview diagram. | Image courtesy of A. Ramirez, A. Kumar, and A. LaFleur, collective MI Crosscutting team

Design particular features into the evaluation systems and tool kits. To serve CCUS technology development and communication with governments and stakeholders, the developed evaluation systems and resulting tool kits should be designed with specific features. First, the systems and tool kits need to be interactive, with feedback loops between system evaluation and technology development, and technology targets to serve overarching goals for carbon reduction and elimination. This is especially important for early-stage R&D such as CCUS. Second, the CCUS tool kits should be designed with interfaces (both hard and soft links) to process tools based on fundamental theories—such as energy balance, thermodynamics, and conservation of mass—that work with existing simulation and optimization models. It is critical that decision makers also understand the full impacts of the technology pathways on a national and regional level. Tool kit development should also include creating tools to assess impacts at the national and regional levels, including interaction with the various energy demand and supply sectors of the economy of a jurisdiction. Finally, case summaries of issues considered in selecting technologies for real public projects would provide an important database for early-phase (low-TRL) research.

Technology Impacts

Successful deployment of CCUS technology requires the ability to match technologies with specific opportunities. Deployment opportunities carry a unique set of technical, economic, and commercial premises that need to be optimized while risks are managed sufficiently. Providing guidance via a globally consistent evaluation system can enhance innovation by identifying these synergistic connections between concepts and technologies in earlier phases of the technology development funnel. This type of screening allows for more focused early-phase technology investments that maximize available funding and promote fit-for-purpose solutions.

There is often a disconnect between early-phase technology development research goals and deployment opportunity challenges, as evaluations typically occur in later project phases. Providing tools and feedback mechanisms to evaluate technologies in early-phase research increases transparency and provides a common understanding across the full technology development spectrum. This ultimately increases the efficiency and effectiveness of the R&D process by accelerating discovery science, enabling early-stage technology prioritization, and encouraging specific R&D targets. This type of system evaluation also showcases the benefits of interdisciplinary research, which can be extended to evaluation of technologies beyond those related to CCUS.

It is critical that decision makers also understand the full impact of technology pathways on a national and regional level. Tool kit development should also include tools for assessing impacts at the national and regional levels, including interaction with the various energy demand and supply sectors of the economy of a jurisdiction.

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6. Conclusion

To meet the goal of stabilizing global atmospheric CO_2 concentrations will require enormous reductions in CO_2 emissions. Although alternate energy sources that release no carbon into the atmosphere—solar, wind, geothermal, hydro, and nuclear power—can reduce global CO_2 emissions, many energy and industrial processes will continue to emit carbon into the atmosphere for the foreseeable future. Indeed, the adoption of these alternative energy sources will take considerable time, adding to the urgency of developing new approaches for CCUS. Thus, to realize the goal of capping the environmental concentrations of CO_2 while the demands for energy continue to increase, there is a critical need for next-generation concepts that will provide efficient and cost-effective technologies for CCUS in the future.

The CCUS workshop participants recognized that the challenges for efficient CCUS will not be met by simple incremental improvements in today's technologies. They were charged with identifying fundamental research needs and opportunities that would provide the underpinning knowledge that is needed to make significant advances in CCUS. The workshop was attended by more than 250 scientists from universities, national laboratories, and industry, as well as representatives from a number of participating Mission Innovation countries.

The goal of the workshop was to assess current gaps in CCUS technologies and identify the most promising basic research directions (Priority Research Directions, or PRDs) that are needed to achieve long-term global carbon management. These PRDs include opportunities for understanding and improving materials, chemical processes, and other scientific and technical areas required to transform next-generation technologies required for efficient and cost-effective management of carbon emissions. Three panels were formed corresponding to the core topics of Capture, Utilization, and Storage. A fourth panel, Crosscutting, assesses research directions that are common to the three core topics.

One major topic examined by the Capture panel for removing CO_2 from effluent streams focused on the need for the development of highly efficient and selective separation methods, ranging from solvent-based sorbent methods to new membranes and solid sorbent systems. The panel identified the need to design new high-performing solvents for CO_2 capture, as well as develop new approaches to incorporate these solvents into environmentally friendly processes. It was recognized that recent advances in computational tools will enable researchers to predict and understand the chemical and physical properties necessary to design potential liquid sorbents. Similarly, the panel acknowledged that advances in materials science and computational methods will enable the design of a new generation of highly selective solid sorbents. This knowledge, combined with multiscale experimental and computational studies, will enable the fundamental understanding needed to design effective sorbent systems, such as those used in chemical looping.

Membrane technologies, both polymeric and inorganic, possess considerable potential for CO_2 separation. The Capture panel emphasized that there are currently major gaps in our understanding of transport phenomena in membrane materials that represent a technical bottleneck for developing next-generation membranes. Armed with this knowledge, however, it would be possible to design membrane structures that are vastly more selective and robust than today's membranes. The Capture panel also examined next-generation combustion concepts, particularly those conducted at extremes of temperature and pressure, to increase the efficiency of combustion and dramatically reduce the formation of CO_2. Advances in understanding these complex processes under these extreme regimes are critical to the development of new combustion technologies. This information is also needed to enable the development of new materials capable of operating under these conditions. Finally, the panel noted that advances in concepts for the carbon-free production of hydrogen from fossil fuels require deeper understanding in combustion-related processes.

Conversion and hydrogenation of CO_2 into high-value chemicals and materials represent major routes for utilization of CO_2. The Utilization panel identified the need to understand fundamental molecular-level processes involved in CO_2 conversion, noting that new computational and in situ characterization tools are needed to gain this understanding. With this knowledge, new catalytic processes—including those based on thermochemical, electrochemical, photochemical and biological processes—could be developed to efficiently convert CO_2 into valuable chemicals and materials. Conversion processes could also be designed to mineralize carbon to facilitate permanent storage of CO_2. For example, processes could be formulated to react CO_2 with various oxides (e.g., Ca, Mg, or Fe) to form stable solid carbonates or to enhance recovery of targeted materials from mining processes. Fundamental understanding of the processes involved in these mineralization processes is needed to improve their overall efficiencies and, therefore, large-scale application. In all of these CO_2 conversion processes, reactions occur at the interfaces of solid–liquid–gas systems, and deeper understanding of these myriad processes at the molecular and atomic scales are needed if CO_2 utilization is to reach its full potential.

Subsurface storage represents the only viable approach to isolating large volumes of CO_2 from the atmosphere and was the focus of the Storage panel. The injection of CO_2 into a subsurface brine-filled aquifer requires detailed knowledge, across broad time scales and length scales, of gas–liquid and gas–solid interactions and other multiphysics processes to increase subsurface capacities. In addition, the panel noted that substantial gaps in knowledge exist in the coupled problem of pressure and geomechanics in various subsurface systems. This is a challenging multiscale problem that requires understanding of fracturing mechanisms in the near-well environment to optimize injection of CO_2. Another area identified by the Storage panel is the need to enhance the direct detection and measurement of CO_2 in deep formations to ensure long-term geological containment is achieved. The panel identified a number of measurements that are required to meet the needs of deep geological storage of CO_2 and noted that next-generation analytical tools and sensors, along with monitoring plans, are needed. The resulting monitoring systems will require the development of computational tools to integrate, interpret, and use large, complex, multidimensional data sets to ensure the integrity of the stored CO_2. The Storage panel also identified the need to forecast and manage induced seismicity with higher fidelity, including gaining fundamental knowledge of fault and fracture systems and developing robust methods for forecasting seismic risks. For example, the panel noted that fundamental knowledge is critically needed to develop proactive mitigation systems that can be used to inform real-time decisions during operations. Further, the panel noted that techniques are needed to interrogate the state of wells—both existing and abandoned—to ensure their integrity and to develop effective remediation technologies. This panel recognized that the issues faced in subsurface storage require multidisciplinary approaches, combined with advances in experiment, computation, data analytics, and characterization.

In addition to the Capture, Utilization, and Storage Panels, a Crosscutting panel was formed to examine themes that would enable all three areas. The need for whole-system analysis across broad length and time scales was repeated in each panel. In particular, the Crosscutting panel identified technoeconomic analysis (TEA) and life cycle analysis (LCA) as critical tools for guiding and prioritizing research because, by its very nature, CCUS is a highly integrated system in which the large magnitude of the technical issues must be assessed in the context of costs and effectiveness. Currently, TEA and LCA models and tools for CCUS are in their early stages. Advances in machine learning and artificial intelligence could be invaluable for assessing the complex systems involved in CCUS. Such information could provide insight from the molecular/atomic scales and ultimately to the macroscopic level of integrated commercial processes. To inform these models, however, new fundamental experimental data are needed to provide this information—from laboratory- to field-scale measurements, as well as data from computational modeling/simulation. The Crosscutting panel also emphasized the need for integration of experiment, simulation, and machine learning across multiple length scales to guide materials discovery and process development. Further, they pointed out that multidisciplinary basic science and engineering research is central for realizing intensified carbon capture, purification, transport, utilization and storage processes. Finally, the Crosscutting panel noted that it is critical to include social aspects in the decision-making process in CCUS, developing tools to integrate TEA, LCA, and social considerations to guide technology optimization.

As the four technical panels concluded their deliberations, they were charged to identify the most promising research directions that could be pursued by the international community. These PRDs, listed in Table 1 of the Executive Summary, are not meant to be prescriptive and all-inclusive. Rather, they are designed to inspire multidisciplinary research teams of scientists and engineers from around the globe to elucidate the foundational chemical and physical phenomena that underpin CCUS. Using this knowledge, today's technology bottlenecks will be overcome and a new generation of CCUS technologies will be catalyzed. These PRDs will yield the design of new materials, novel chemical and physical processes, and new sensors and characterization and computational tools that will make CCUS processes more efficient, reliable, and cost-effective. The workshop participants acknowledged that the challenges of CCUS are daunting, but they were confident that research addressing the identified PRDs holds enormous promise for reaching the goal of stabilizing global CO_2 levels. This critically important research will result in breakthroughs needed to design effective, scalable, and economical technologies for CCUS, addressing a major worldwide challenge as energy demands increase—increased global production of CO_2 and the associated harmful impacts of climate change.

Acknowledgments

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Our special appreciation goes to Dr. Grace Bochenek, director of the National Energy Technology Laboratory (US); and Khalid Abuleif, senior advisor, chief negotiator for Climate Agreements (Saudi Arabia) for their valuable insights and leadership during the workshop. As the co-leads of the Carbon Capture Challenge, Dr. Tidjani Niass, Hamoud Otaibi (Saudi Arabia), Jordan Kislear, John Litynski, Sarah Forbes, and Stephanie Duran (US-DOE) provided overall leadership and steering for the workshop.

We extend our special thanks to our distinguished workshop co-chairs: Michelle Buchanan, Oak Ridge National Laboratory (United States), served as the workshop chair. Dr. Jørild Svalestuen, Gassnova (Norway) led the CO_2 capture panels; Dr. Alissa Park, Columbia University, (United States) led the CO_2 utilization panels; Dr. Don DePaolo, Lawrence Berkeley National Laboratory (United States) led the CO_2 storage panels; and Dr. Joe Powell, Shell (United States) led the crosscutting panels.

Our appreciation goes also to our panel co-leads.

- For CO_2 capture: Gary Rochelle and Mohammed Abu Zhara (Solvents); Mohamed Eddaoudi and Jochen Strohle (Sorbents and Looping Systems); Earl Goetheer and Rune Gredesen (Membranes); Jon Gibbins and Robin Hughes (Combustion and Other Technologies)
- For CO_2 utilization: Peter Styring and Rebecca Boudreaux (Thermochemical Conversion and Hydrogenation of CO_2); Tom Jaramillo and Marc Robert (Electrochemical and Photochemical Conversion of CO_2); Eric Kennedy and Giulia Costa (CO_2 Conversion to Solid Carbonates); Marc Strous and Greg Stephanopoulus (Biological Conversion of CO_2)
- For CO_2 storage: Philip Ringrose and Curt Oldenburg (Injectivity and Capacity); Ziqui Xue and Jonathan Pearce (Monitoring, Verification and Performance Metrics); David Eaton and Hideo Aochi (Forecasting and Managing Induced Seismicity); Franz May and Rick Chalaturnyk (Well Integrity)
- For Crosscutting, Dr. Jay Lee (Korea Advanced Institute of Science and Technology) and Dr. Andrea Ramirez (TU Delft)

Our special thanks go to Brenda Wyatt of Oak Ridge National Laboratory, who spent tremendous effort in numerous administrative and communication tasks associated with the preparation of the workshop and its report.

APPENDIX A: WORKSHOP PARTICIPANTS

Mission Innovation Carbon Capture, Uilization, and Storage Experts' Workshop

Participants

Last Name	First Name	Institution	Role	Focus Area / Panel
Abu Zahra	Mohammed	Masdar Institute–Khalifa University	Panel Lead	CAPTURE—Solvents
Abuleif	Khalid	Climate Change, Ministry of Energy, Industry and Mineral Resources	Observer	
Adderley	Bruce	University of Sheffield	Participant	UTILIZATION—CO_2 Conversion to Solid Carbonates
Al Yafei	Arafat	ADNOC–ENP	Observer	
Al-Bahily	Khalid Abdullah	Sabic	Participant	UTILIZATION—Thermochemical Conversion and Hydrogenation of CO_2
Al-Marzouqi	Mohamed	United Arab Emirates University	Participant	CAPTURE—Sorbents and Looping Systems
Al-Sherehy	Fahad	SABIC	Observer	
Albassam	Abdulrahman	Saudi Aramco	Participant	CROSSCUT
AlHafedh	Yousef	Member of Steering Committee for Mission Innovation	Observer	
Allada	Ramakumar	SABIC	Participant	CAPTURE—Sorbents and Looping Systems
Allam	Rodney	8Rivers Capital and NET Power	Participant	CAPTURE—Combustion and Other Technologies
Allison	Brian	Department for Business, Energy and Industrial Strategy	Observer	Government
AlOtaibi	Hamoud	Advisor, Climate Change, Ministry of Energy, Industry and Mineral Resources	Observer	
AlQuraishi	Abddularahman	King Abdulaziz City for Science and Technology	Participant	STORAGE—Injectivity and Capacity
Alshehri	Ammar	Saudi Aramco	Participant	STORAGE—Monitoring, Verification and Performance Metrics
Alshihri	Saeed	King Abdulaziz City for Science and Technology	Participant	UTILIZATION—Thermochemical Conversion and Hydrogenation of CO2
Aochi	Hideo	Geology Laboratory of Ecole Normale Superieure	Panel Lead	STORAGE—Forecasting and Managing Induced Seismicity
Aresta	Michele	IC2R srl	Participant	UTILIZATION—Biological Conversion of CO2

Last Name	First Name	Institution	Role	Focus Area / Panel
Armstrong	Katy	University of Sheffield/ CDU UK	Participant	UTILIZATION—Thermochemical Conversion and Hydrogenation of CO2
Atwater	Harry	California Institute of Technology	Participant	UTILIZATION—Electrochemical and Photochemical Conversion of CO2
Baek	San Joo	KETEP	Observer	
Baker	Richard	MTR	Participant	CAPTURE—Membranes
Ballivet-Tkatchenko	Danielle	CNRS	Participant	UTILIZATION—Thermochemical Conversion and Hydrogenation of CO2
Banta	Scott	Columbia University	Participant	UTILIZATION—Biological Conversion to CO2
Bar-Even	Arren	Max Planck Institute of Molecular Plant Physiology (Germany)	Participant	UTILIZATION—Biological Conversion of CO2
Barrett	Andrew	Geoscience, Australia	Observer	Government
Beaudoin	Georges	Université Laval	Participant	UTILIZATION—CO2 Conversion to Solid Carbonates
Benemann	John	MicroBio Engineering Inc. USA	Participant	UTILIZATION—Biological Conversion of CO2
Bergerson	Joule	University of Calgary	Participant	CROSSCUT
Berghout	Niels	International Energy Agency	Observer	
Berlinguette	Curtis	University of British Columbia	Participant	UTILIZATION—Electrochemical and Photochemical Conversion of CO2
Bevan	Nick	Department for Busisness, Energy and Industrial	Participant	CAPTURE—Solvents
Bielicki	Jeff	The Ohio State University	Participant	CROSSCUT
Bocarsly	Andy	Princeton University	Participant	UTILIZATION—Electrochemical and Photochemical Conversion of CO2
Bochenek	Grace	National Energy Technology Laboratory	Observer	
Bonnetblanc	Paul	Ministry for an Ecological and Solidary Transition	Participant	OBSERVER
Boudreaux	Rebecca	Oberon Fuels	Panel Lead	UTILIZATION—Thermochemical Conversion and Hydrogenation of CO2
Bourgeois	Florent	University of Toulouse–Laboratoire déGenie Chimique	Participant	UTILIZATION—CO2 Conversion to Solid Carbonates
Bredesen	Rune	Sintef Materials and Chemistry	Panel Lead	CAPTURE—Membranes
Brennecke	Joan	University of Notre Dame	Participant	CAPTURE—Solvents

Last Name	First Name	Institution	Role	Focus Area / Panel
Brickett	Lynn	US Department of Energy	Observer	
Bromhal	Grant	US Department of Energy	Participant	STORAGE—Well Diagnostics
Buchanan	Michelle	Oak Ridge National Laboratory	Chair	
Campbell	Matthew	Shell Cansolv	Participant	CAPTURE—Solvents
Cantat	Thibault	CEA	Participant	UTILIZATION—Thermochemical Conversion and Hydrogenation of CO2
Carey	Jeremy	42 Technology	Participant	CAPTURE—Combustion and Other Technologies
Carey	Bill	Los Alamos National Laboratory	Participant	STORAGE—Well Diagnostics
Chalaturnyk	Rick	University of Alberta	Panel Lead	STORAGE—Well Diagnostics
Chiang	Pen-Chi	National Taiwan University	Participant	UTILIZATION—CO2 Conversion to Solid Carbonates
Chiarabba	Claudio	INGV	Participant	STORAGE—Forecasting and Managing Induced Seismicity
Chui	Eddy	Natural Resources Canada, CanmetENERGY	Observer	
Costa	Giulia	University of Rome–Tor Vergata	Panel Lead	UTILIZATION—CO2 Conversion to Solid Carbonates
Cutter	Amy	Department for Business, Energy and Industrial Strategy	Observer	Government
Dairaneih	Issam	CO2 Sciences	Participant	UTILIZATION—CO2 Conversion to Solid Carbonates
DePaolo	Don	Lawrence Berkeley National Laboratory/University of California–Berkeley	Co-Chair	STORAGE
Dibble	Robert	King Abdullah University of Science and Technology	Participant	CAPTURE—Combustion and Other Technologies
Dipple	Greg	University of British Columbia	Participant	UTILIZATION—CO2 Conversion to Solid Carbonates
Dipple	Greg	University of British Columbia	Participant	UTILIZATION—Engineering Complex Interfaces for Enhancing Hydrocarbon Recovery with Carbon Storate
Ditaranto	Mario	Sintef	Participant	CAPTURE—Combustion and Other Technologies
Dixon	Tim	IEAGHG	Participant	CROSSCUT
Dodds	Kevin	ANLECRD	Participant	STORAGE—Monitoring, Verification and Performance Metrics

Last Name	First Name	Institution	Role	Focus Area / Panel
Dufaud-Niccolai	Véronique	University of Lyon	Participant	UTILIZATION—Thermochemical Conversion and Hydrogenation of CO2
Duguid	Andrew	Battelle	Participant	STORAGE—Well Diagnostics
Eaton	David	University of Calgary	Panel Lead	STORAGE—Forcasting and Managing Induced Seismicity
Eddaoudi	Mohamed	King Abdullah University of Science and Technology	Panel Lead	CAPTURE—Sorbents and Looping Systems
Eide	Lars Ingolf	Research Council of Norway	Deputy Co-Chair	CAPTURE
Einbu	Aslak	Sintef Materials and Chemistry	Participant	CAPTURE—Solvents
Ekendahl	Susanne	RISE Research Institutes of Sweden	Participant	UTILIZATION—Biological Conversion of CO2
El Khamlichi	Aïcha	ADEME	Participant	CROSSCUT
Eliasson	Jon Peder	Sintef	Participant	STORAGE—Monitoring, Verification and Performance Metrics
Eritsland	Siri	Norweigan Ministry of Petroleum and Energy	Observer	
Fan	Liang-Shih	The Ohio State University	Participant	CAPTURE—Sorbents and Looping Systems
Fennell	Paul	Imperial College	Participant	CAPTURE—Sorbents and Looping Systems
Ferrari	Maria-Chiara	University of Edinburgh	Participant	CAPTURE—Membranes
Forbes	Sarah	US Department of Energy, Office of Clean Coal and Carbon Management	Observer	Government
Fourage	Laurent	Total	Participant	UTILIZATION—Biological Conversion of CO2
Freeman	Benny	University of Texas–Austin	Participant	CAPTURE—Membranes
Freifeld	Barry	Lawrence Berkeley National Laboratory	Participant	STORAGE—Monitoring, Verification and Performance Metrics
Fujita	Etsuko	Brookhaven National Laboratory	Participant	UTILIZATION—Electrochemical and Photochemical Conversion of CO2
Gadikota	Greeshma	University of Wisconsin–Madison	Participant	STORAGE—Injectivity and Capacity
Gadikota	Greeshma	University of Wisconsin–Madison	Panel Lead	UTILIZATION—Engineering Complex Interfaces for Enhancing Hydrocarbon Recovery with Carbon Storate
Gaertner	Lars-Erik	Linde Group	Participant	UTILIZATION—CO2 Conversion to Solid Carbonates
Garcia Lopez	Susana	Heriot-Watt University	Participant	CAPTURE—Sorbents and Looping Systems

Last Name	First Name	Institution	Role	Focus Area / Panel
Gasda	Sarah	UNI	Participant	STORAGE—Injectivity and Capacity
Gentry	Randall	Deputy Director, National Energy Technology Laboratory/Department of Energy	Observer	
Geuzebroek	Frank	Gasco	Participant	CAPTURE—Solvents
Gibbins	Jon	University of Sheffield/UKCCSRC	Panel Lead	CAPTURE—Combustion and Other Technologies
Girguis	Peter	Harvard	Participant	UTILIZATION—Biological Conversion of CO2
Gleeson	Michael	DIFFER	Participant	UTILIZATION—Thermochemical Conversion and Hydrogenation of CO2
Goetheer	Earl	TNO–Netherlands	Panel Lead	CAPTURE—Membranes
Grace	John	University of British Columbia and Carbon Capture and Conversion Institute	Participant	CAPTURE—Sorbents and Looping Systems
Greenberg	Sallie	Illinois State Geological Survey	Participant	CROSSCUT
Gulen	John	Bechtel	Participant	CAPTURE—Combustion and Other Technologies
Guo	Ying	IRIS	Participant	STORAGE—Well Diagnostics
Gupta	Raghubir	Research Triangle Institute	Participant	CAPTURE—Sorbents and Looping Systems
Hahn	Christopher	SUNCAT/SLAC	Participant	UTILIZATION—Electrochemical and Photochemical Conversion of CO2
Hamad	Esam	Saudi Aramco	Participant	CAPTURE—Sorbents and Looping Systems
Hansen	John Bogild	Haldor Topsøe A/S	Participant	UTILIZATION—Electrochemical and Photochemical Conversion of CO2
Haq	Zia	Department of Energy	Observer	
Harold	Michael	University of Houston	Participant	UTILIZATION—Thermochemical Conversion and Hydrogenation of CO2
Haszeldine	Stuart	University of Edinburgh/SCCS	Participant	CROSSCUT
He	Liangnian	Nankai University	Participant	UTILIZATION—Thermochemical Conversion and Hydrogenation of CO2
Heldebrant	David	Pacific Northwest National Laboratory	Participant	CAPTURE—Solvents

Last Name	First Name	Institution	Role	Focus Area / Panel
Heller	Claude	Air-Liquide	Participant	UTILIZATION—Electrochemical and Photochemical Conversion of CO2
Henni	Amr	University of Regina	Participant	CAPTURE—Solvents
Heron	Ted	TCGR CO2CC Program	Observer	
Herzog	Howard	Massachusetts Institute of Technology	Participant	CROSSCUT
Hills	Tom	Calix Limited	Participant	CAPTURE—Sorbents and Looping Systems
Hoff	Karl Anders	SINTEF	Participant	CAPTURE—Solvents
Hovorka	Sue	Bureau of Economic Geology, University of Texas–Austin	Participant	STORAGE—Monitoring, Verification and Performance Metrics
Huesemann	Michael	Pacific Northwest National Laboratory	Participant	UTILIZATION—Biological Conversion of CO2
Hughes	Robin	CanmetENERGY, Natural Resources Canada	Panel Lead	CAPTURE—Combustion and Other Technologies
Ip	Alex	University of Toronto	Participant	UTILIZATION—Electrochemical and Photochemical Conversion of CO2
Jamal	Aqil	Saudi Aramco	Participant	CAPTURE—Solvents
Jaramillo	Thomas	Stanford University	Panel Lead	UTILIZATION—Electrochemical and Photochemical Conversion of CO2
Jayaweera	Indira	SRI International	Participant	CAPTURE—Membranes
Jenvey	Nigel	BP	Participant	STORAGE—Monitoring, Verification and Performance Metrics
Jiao	Feng	Delaware	Participant	UTILIZATION—Electrochemical and Photochemical Conversion of CO2
Jordan	Elizabeth	SABIC	Observer	
Kay	John	Energy and Environmental Research Center	Participant	CAPTURE—Solvents
Kelly	Robert	North Carolina State University	Participant	UTILIZATION—Biological Conversion of CO2
Kemper	Jasmin	IEAGHG	Participant	CROSSCUT
Kenis	Paul	UIUC	Participant	UTILIZATION—Electrochemical and Photochemical Conversion of CO2
Kennedy	Eric	University of Newcastle Australia	Panel Lead	UTILIZATION—CO2 Conversion to Solid Carbonates
Khiavi	Soheil	Inventysinc	Participant	CAPTURE—Sorbents and Looping Systems

Last Name	First Name	Institution	Role	Focus Area / Panel
Kislear	Jordan	US Department of Energy, Office of Clean Coal and Carbon Management	Observer	
Koros	William	Georgia Institute of Technology	Participant	CAPTURE—Membranes
Kougionas	Vassilioas	European Commission	Observer	
Krevor	Sam	Imperial College London	Participant	STORAGE—Injectivity and Capacity
Kulkarni	Sudhir	Air Liquide	Participant	CAPTURE—Membranes
Kumar	Amit	University of Alberta	Participant	CROSSCUT
Kurosawa	Atsushi	Institute of Applied Energy	Participant	UTILIZATION—Electrochemical and Photochemical Conversion of CO2
Kusuma	Victor	National Energy Technology Laboratory	Observer	
LaFleur	Aimee	Shell	Participant	CROSSCUT
Lail	Marty	RTI Int.	Participant	UTILIZATION—Thermochemical Conversion and Hydrogenation of CO2
Larring	Yngve	SINTEF	Participant	CAPTURE—Sorbents and Looping Systems
Lawton	Don	University of Calgary	Participant	STORAGE—Forecasting and managing Induced seismicity
Leclaire	Julien	University of Lyon	Participant	CAPTURE—Solvents
Lee	Jay	KAIST	Panel Lead	CROSSCUT
Legallo	Yann	Geogreen	Participant	STORAGE—Injectivity and Capacity
Lesemann	Markus	RTI	Participant	CAPTURE—Solvents
Litynski	John	US Department of Energy, Office of Fossil Energy	Observer	
Lucquaiud	Mathieu	University of Edinburgh	Participant	CAPTURE—Solvents
Ma	Xinbin	Tianjin University	Panel Lead	UTILIZATION—Thermochemical Conversion and Hydrogenation of CO2
Mac Dowell	Niall	Imperial College London	Participant	CROSSCUT
Mahurin	Shannon	ORNL	Participant	CAPTURE—Membranes
Martin	Greg	University of Melbourne	Participant	UTILIZATION—Biological Conversion of CO2
Masel	Richard	Dioxide Materials	Participant	UTILIZATION—Electrochemical and Photochemical Conversion of CO2
Matuszewski	Mike	US Department of Energy	Participant	CROSSCUT
May	Franz	BGR	Panel Lead	STORAGE—Well Diagnostics
Meckel	Tip	Gulf Coast Carbon Center–TX BEG	Participant	STORAGE—Monitoring, Verification and Performance Metrics

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Merment	Alain	French Embassy	Observer	
Monkman	Sean	CarbonCure Technologies	Participant	UTILIZATION—CO2 Conversion to Solid Carbonates
Morton	Frank	Southern Company	Observer	
Moser	Peter	RWE	Participant	UTILIZATION—Electrochemical and Photochemical Conversion of CO2
Munson	Ron	Global CCS Institute	Observer	
Murphy	John	TCGR CO2CC Program	Observer	
Neele	Filip	TNO/ZEP	Participant	STORAGE—Injectivity and Capacity
Nevicato	David	Total	Participant	CAPTURE—Sorbents and Looping Systems
Niass	Tidjani	Saudi Aramco	Observer	
Nottvedt	Arvid	CMR	Participant	STORAGE—Injectivity and Capacity
O'brien	Simon	Shell Canada	Participant	STORAGE—Forecasting and Managing Induced Seismicity
Oldenburg	Curt	Lawrence Berkeley National Laboratory	Panel Lead	STORAGE—Injectivity and Capacity
Oliver	Tim	University of Newcastle	Participant	UTILIZATION—CO2 Conversion to Solid Carbonates
Onarheim	Kristin	VTT Technical Research Centre	Participant	UTILIZATION—Thermochemical Conversion and Hydrogenation of CO2
Palmore	Tayhas	Brown University	Participant	UTILIZATION—Electrochemical and Photochemical Conversion of CO2
Park	Alissa	Columbia	Co-Chair	UTILIZATION
Park	Jin-Won		Participant	CAPTURE—Solvents
Park	Youngjune	GIST Korea	Participant	UTILIZATION—CO2 Conversion to Solid Carbonates
Park	Sang-Eon	Inha University	Participant	UTILIZATION—Thermochemical Conversion and Hydrogenation of CO2
Park	Alissa	Columbia University	Participant	UTILIZATION—Engineering Complex Interfaces for Enhancing Hydrocarbon Recovery with Carbon Storate
Parkin	Gerard	Columbia University	Participant	UTILIZATION—Thermochemical Conversion and Hydrogenation of CO2

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Pasquier	Luis-César	INRS-ETE, University of Quebec	Participant	UTILIZATION—CO2 Conversion to Solid Carbonates
Pasquier	Louis-Cesar	INRS-ETE, University of Quebec	Participant	UTILIZATION—Engineering Complex Interfaces for Enhancing Hydrocarbon Recovery with Carbon Storate
Pearce	Jonathan	BGS, UK	Panel Lead	STORAGE—Monitoring, Verification and Performance Metrics
Peters	Thijs	Sintef Materials and Chemistry	Participant	CAPTURE—Membranes
Pezard	Philippe	Geosciences laboratory in Montpellier	Participant	STORAGE—Well Diagnostics
Plaza	Jorge	SABIC	Participant	CAPTURE—Solvents
Polklas	Thomas	MAN Diesel and Turbo	Participant	CROSSCUT
Powell	Joe	Shell	Co-Chair	CROSSCUT
Prigiobbe	Valentina	Stevens Institute of Technology	Participant	UTILIZATION—CO2 Conversion to Solid Carbonates
Progiobbe	Valentina	Stevens Institute of Technology	Participant	UTILIZATION—Engineering Complex Interfaces for Enhancing Hydrocarbon Recovery with Carbon Storate
Puxty	Graeme	CSIRO Energy	Participant	CAPTURE—Solvents
Raab	Matthias	CO2CRC	Participant	STORAGE—Well Diagnostics
Ramirez	Andrea	TU Delft	Panel Lead	CROSSCUT
Rayner	Chris	Univ of Leeds	Participant	CAPTURE—Solvents
Reiner	David	University of Cambridge	Participant	CROSSCUT
Rigby	Sean	BASF	Participant	CAPTURE—Solvents
Rigollet	Christophe	Géodenergies	Participant	STORAGE—Injectivity and Capacity
Riman	Richard	Rutgers University	Participant	UTILIZATION—CO2 Conversion to Solid Carbonates
Ringrose	Philip	Statoil	Panel Lead	STORAGE—Injectivity and Capacity
Ringrose	Philip	Statoil	Participant	UTILIZATION—Engineering Complex Interfaces for Enhancing Hydrocarbon Recovery with Carbon Storate
Robert	Marc	University of Diderot–Paris 7	Panel Lead	UTILIZATION—Electrochemical and Photochemical Conversion of CO2
Robles	Luis	Total	Participant	CROSSCUT
Rochelle	Gary	University of Texas–Austin	Panel Lead	CAPTURE—Solvents

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Rockey	John	National Energy Technology Laboratory	Observer	
Rodosta	Traci	National Energy Technology Laboratory	Observer	
Røkke	Nils	SINTEF/ZEP	Participant	CAPTURE—Combustion and Other Technologies
Romanak	Katherine	Bureau of Economic Geology, University of Texas	Participant	STORAGE—Monitoring, Verification and Performance Metrics
Rondinone	Adam	Oak Ridge National Laboratory	Participant	UTILIZATION—Electrochemical and Photochemical Conversion of CO2
Rostron	Ben	University of Alberta	Participant	STORAGE—Monitoring, Verification and Performance Metrics
Rostron	Benjamin	University of Alberta	Participant	UTILIZATION—Engineering Complex Interfaces for Enhancing Hydrocarbon Recovery with Carbon Storate
Rufael	Tecle	Chevron	Participant	CROSSCUT
Rutqvist	Jonny	Lawrence Berkeley National Laboratory	Participant	STORAGE—Forecasting and managing Induced seismicity
Sadat	Wajdi	Saudi Aramco	Participant	UTILIZATION—Electrochemical and Photochemical Conversion of CO2
Santos	Rafael	University of Guelph	Participant	UTILIZATION—CO2 Conversion to Solid Carbonates
Sasmaz	Erdem	University of South Carolina	Participant	UTILIZATION—Thermochemical Conversion and Hydrogenation of CO2
Shankar	Santhosh	Shell	Participant	UTILIZATION—Electrochemical and Photochemical Conversion of CO2
Sharova	Natalia	Global CCS Institute	Observer	
Shen	Eric	Exxon Mobil	Observer	
Shi	Caijun	Hunan University	Participant	UTILIZATION—CO2 Conversion to Solid Carbonates
Shi	Yixiang	Tsinghua University	Participant	UTILIZATION—Electrochemical and Photochemical Conversion of CO9
Shimizu	George	University of Calgary	Participant	CAPTURE—Sorbents and Looping Systems
Simpson	Sean	LanzaTech	Participant	UTILIZATION—Biological Conversion of CO2

Last Name	First Name	Institution	Role	Focus Area / Panel
Skeie	Bernt	Prototech	Participant	CAPTURE—Membranes
Skone	Timothy	National Energy Technology Laboratory	Participant	CROSSCUT
Slagtern	Åse	Research Council of Norway	Observer	
Smit	Berend	University of California–Berkeley/EPFL	Participant	CAPTURE—Sorbents and Looping Systems
Song	Chunshan	Pennsylvania State University	Participant	UTILIZATION—Thermochemical Conversion and Hydrogenation of CO2
Stack	Andrew	Oak Ridge National Laboratory	Participant	STORAGE
Stendardo	Stefano	ENEA	Observer	
Stephanopoulos	Greg	Massachusetts Institute of Technology	Panel Lead	UTILIZATION—Biological Conversion of CO2
Stevenson	Don	Director of the Advance Energy Systems group at GTI	Participant	CAPTURE—Combustion and Other Technologies
Stevenson	Scott	SABIC	Participant	UTILIZATION—Thermochemical Conversion and Hydrogenation of CO2
Stolaroff	Joshua	Lawrence Livermore National Laboratory	Participant	CAPTURE—Sorbents and Looping Systems
Ströhle	Jochen	Technical University of Darmstadt	Panel Lead	CAPTURE—Sorbents and Looping Systems
Strous	Marc	University of Calgary	Panel Lead	UTILIZATION—Biological Conversion of CO2
Styring	Peter	University of Sheffield/CDUUK	Panel Lead	UTILIZATION—Thermochemical Conversion and Hydrogenation of CO2
Summers	Mark	Alberta Innovates	Participant	STORAGE—Monitoring, Verification and Performance Metrics
Svalestuen	Jørild	Gassnova	Co-Chair	CAPTURE
Sweetnam	Glen	US Department of Energy, Director, African and Middle Eastern Affairs	Observer	
Tanaka	Ryozo	RITE	Participant	STORAGE—Monitoring, Verification and Performance Metrics
Tang	Junwang	UCL	Participant	UTILIZATION—Electrochemical and Photochemical Conversion of CO2
Thibeau	Sylvain	Total	Participant	STORAGE—Injectivity and Capacity
Torsaeter	Malin	SINTEF-PR	Participant	STORAGE—Well Diagnostics

Last Name	First Name	Institution	Role	Focus Area / Panel
Tran	KC	Carbon CEEnergy	Participant	UTILIZATION—Electrochemical and Photochemical Conversion of CO2
Trautz	Rob	Electric Power Research Institute	Participant	STORAGE—Monitoring, Verification and Performance Metrics
Tuli	D K	Indian Oil	Observer	
Tumas	Bill	National Renewable Energy Laboratory	Participant	UTILIZATION—Electrochemical and Photochemical Conversion of CO2
Unocic	Ray	Oak Ridge National Laboratory	Participant	CROSSCUT
Van der Baan	Mirko	University of Alberta	Participant	STORAGE—Forecasting and Managing Induced Seismicity
Van der Stricht	Wim	European Commission	Participant	UTILIZATION—Biological Conversion of CO2
Van Mechelen	Dirk	ORBIX Belgium	Participant	UTILIZATION—CO2 Conversion to Solid Carbonates
Vente	Jaap	ECN	Participant	UTILIZATION-Thermochemical Conversion and Hydrogenation of CO2
Verdon	James	University of Bristol	Participant	STORAGE—Forecasting and Managing Induced Seismicity
Vesborg	Peter	Technical University of Denmark	Participant	UTILIZATION—Electrochemical and Photochemical Conversion of CO2
Wang	Michael	Argonne National Laboratory	Participant	CROSSCUT
Wang	Tao	Zhejiang University	Participant	UTILIZATION—CO2 Conversion to Solid Carbonates
Wang	Shengping	Tianjin University	Participant	UTILIZATION—Thermochemical Conversion and Hydrogenation of CO2
Wang	Tao	Zhejiang University	Participant	UTILIZATION—Engineering Complex Interfaces for Enhancing Hydrocarbon Recovery with Carbon Storate
Weber	Robert	Pacific Northwest National Laboratory	Participant	UTILIZATION—Biological Conversion of CO2
Webley	Paul	University of Melbourne	Participant	CAPTURE—Sorbents and Looping Systems
Weeks	Brian	Gas Technology Institute	Observer	
Wei	Xiatong (Tony)	SABIC	Participant	CAPTURE—Membranes

Last Name	First Name	Institution	Role	Focus Area / Panel
Wen	Cun	University of South Carolina	Observer	
White	Joshua	Lawrence Livermore National Laboratory	Participant	STORAGE—Forecasting and Managing Induced Seismicity
Whittaker	Steve	Illinois Geological Survey	Participant	STORAGE—Injectivity and Capacity
Wildgust	Neil	UNDEERC	Participant	STORAGE—Well Diagnostics
Wildgust	Neil	University of North Dakota	Participant	UTILIZATION—Engineering Complex Interfaces for Enhancing Hydrocarbon Recovery with Carbon Storate
Williams	Brian	BP	Observer	
Wolfe	Jim	Jupiter Oxygen Corporation	Observer	
Woo	Tom	University of Ottawa	Participant	CAPTURE—Sorbents and Looping Systems
Xue	Ziqiu	RITE	Panel Lead	STORAGE—Monitoring, Verification and Performance Metrics
Younes	Mourad	Saudi Aramco	Participant	CAPTURE—Combustion and Other Technologies
Zhou	Sean	GreenOre	Participant	UTILIZATION—CO2 Conversion to Solid Carbonates
Zhou	Sean	Columbia University	Participant	UTILIZATION—Engineering Complex Interfaces for Enhancing Hydrocarbon Recovery with Carbon Storate

APPENDIX B: WORKSHOP AGENDA

Mission Innovation Carbon Capture, Utilization and Storage Experts' Workshop

Hilton Hotel North, Houston Texas
September 25–29, 2017

Monday, September 25, 2017

6:00 – 7:00 p.m.	Social Hour (Invitation Only) Co-Hosts, Co-Chairs, Panel Leads Location: Donatello
7:00 – 8:00 p.m.	Dinner (Invitation Only) Welcome, Introductions, Workshop Plan/Logistics Co-Hosts, Co-Chairs, Panel Leads Location: Donatello

Tuesday, September 26, 2017

7:00 – 8:00 a.m.	Workshop Registration/Breakfast Location: Raphael AB Foyer

Opening Plenary Session – Raphael AB

8:00 – 8:30 a.m.	Welcome – Workshop Co-Sponsors Dr. Randy Gentry, Deputy Director, National Energy Technology Laboratory, U S Department of Energy Khalid Abuleif, Sr. Advisor, Chief Negotiator for Climate Agreements, Ministry of Energy, Industry and Mineral Resources, Saudi Arabia
8:30 – 8:45 a.m.	Mission Innovation Overview Tidjani Niass, Ministry of Energy, Industry and Mineral Resources, Saudi Arabia
8:45 – 9:15 a.m.	Chair Welcome, Workshop Charge/Structure and Co-Chair Introductions Michelle Buchanan, Oak Ridge National Laboratory
9:15 – 10:15 a.m.	Topic Overview and Panel Introductions – Workshop Co-Chairs (15 min. each) Jørild Svalestuen – Capture Alissa Park – Utilization Don DePaolo – Storage Joe Powell – Crosscut
10:15 – 10:20 a.m.	Closing Remarks and Panel Instructions Michelle Buchanan
10:20 – 10:30 a.m.	Refreshment Break
10:30 – Noon	Theme/Focus Area Parallel Sessions: align, discuss interfaces, and other issues relevant to the panels Capture – Location: Donatello Utilization – Location: Raphael C Storage – Location: Raphael D Crosscut – Location: Galileo I & II

12:00 – 1:30 p.m.	Working Lunch Location: Raphael AB Foyer
1:30 – 5:00 p.m.	Organize into parallel panel sessions Locations: See last page of Agenda
3:00 - 4:00 p.m.	Refreshments available Panels continue working; break at your leisure Location: Outside of panel locations
4:30 – 5:00 p.m.	Technical Committee Meeting (Invitation Only) Review workshop proceedings, change to panels, logistics, and other issues Location: Board Room
5:30 – 7:00 p.m.	Opening Reception Location – Alfresco
7:00 – 9:00 p.m.	Parallel Panel Discussions continue – OPTIONAL Locations: See last page of agenda

Wednesday, September 27, 2017

7:00 - 8:00 a.m.	Breakfast Location: Raphael AB Foyer
8:00 – 9:30 a.m.	Parallel Plenary Sessions for Focus Areas (Chair, Co-chairs, Panel Leads, and Panel Participants review PRDs) Capture – Location: Donatello Utilization – Location: Raphael C Storage – Location: Raphael D Crosscut – Location: Galileo I & II
9:30 – 10:00 a.m.	Break
10:00 – 10:40 a.m.	Mission Innovation Updates (20 minutes each) Business/Investor Engagement Group MI Challenge Group Jordan Kislear and Tidjani Niass Location: Raphael AB
10:40 – Noon	Plenary Session Co-Chairs Report Out (e.g., progress, issues) – 20 min. each with 5 min. intro Jørild Svalestuen – Capture Alissa Park – Utilization Don DePaolo – Storage Joe Powell – Crosscut Location: Raphael AB
12:00 - 5:00 p.m.	Panels/PRD Discussions (continue) Locations: See last page of agenda
12:00 – 1:30 p.m.	Working Lunch Location: Outside of panel locations
3:00 – 4:00 p.m.	Refreshments available (Panels continue working; break at your leisure) Location: Outside panel locations

4:30 – 5:00 p.m.	Technical Committee Meeting (Invitation Only) Review workshop proceedings, change to panels, logistics, and other issues Location: Board Room
5:00 – 6:00 p.m.	Break
6:00 – 8:00 p.m.	Workshop Dinner Location: Raphael AB

<u>Thursday, September 28, 2017</u>

7:00 – 8:00 a.m.	Breakfast Location: Raphael AB Foyer
8:00 – 10:00 a.m.	Panel Discussions/PRDs refined (continued) Locations: See last page of Agenda
8:00 – 9:30 a.m.	MI Steering Committee Meeting/Call (Invitation Only) Discuss next steps for report, CCUS Challenge Next Steps, focus and direction, and other Committee Business
10:00 – 10:30 a.m.	Break
10:30 – 11:30 a.m.	Panel Discussions/PRDs Refined (continued)
11:30 – 12:30	Lunch Location: Raphael AB
12:30 – 2:30 p.m.	Plenary Session Report out from o-Chairs on Theme/Focus Areas (30 min. each) Jørild Svalestuen – Capture Alissa Park – Utilization Don DePaolo – Storage Joe Powell – Crosscut Location: Raphael AB
2:30– 2:45 p.m.	Summary of Workshop and Next Steps Michelle Buchanan
2:45 – 3:15 p.m.	Closing Remarks – US and Saudi Arabia Workshop Chairs
3:15 p.m.	Workshop Adjourned
3:30 – 5:30 p.m.	Crosscutting Panel Group Meeting Location: Raphael D
3:30 – 5:30 p.m.	Co-Chairs, Panel Leads and Lead Authors begin writing session Location: Raphael C
5:30 p.m.	Dinner – On your own

<u>Friday, September 29, 2017</u>

Attendance by Invitation Only

7:30 – 8:30 a.m.	Breakfast Location: Raphael C
8:30 – 12:30	Writing sessions (Invitation Only Location: Raphael C
12:30 p.m.	Lunch available/continue writing
3:00 p.m.	Adjourn

Parallel Panel Sessions

Theme/Focus Area 1: CO_2 Capture (C) Jørild Svalestuen (NOR), Co-Chair

Panel C1: Solvents – Raphael C
Panel Leads: Gary Rochelle (USA) and Mohammed Abu Zhara (UAE)

Panel C2: Sorbents and Looping Systems – Raphael D
Panel Leads: Mohamed Eddaoudi (SAU) and Jochen Ströhle (DEU)

Panel C3: Membranes – Campobello
Panel Leads: Earl Goetheer (NLD) and Rune Bredesen (NOR)

Panel C4: Combustion and Other Technologies – Galileo II
Panel Leads: Jon Gibbins (UK) and Robin Hughes (CAN)

Theme/Focus Area 2: CO_2 Utilization (U) Alissa Park (USA), Co-Chair

Panel U1: Thermochemical Conversion and Hydrogenation of CO_2 – Room 1
Panel Leads: Peter Styring (UK), Xinbin Ma (CHN), Rebecca Boudreaux (USA)

Panel U2: Electrochemical and Photochemical Conversion of CO_2 – Room 2
Panel Leads: Tom Jaramillo (USA) and Marc Robert (FRA)

Panel U3: CO_2 Conversion to Solid Carbonates – Room 3
Panel Leads: Eric Kennedy (AU) and Giulia Costa (ITA)

Panel U4: Biological Conversion of CO_2 – Donatello
Panel Leads: Marc Strous (CAN) and Greg Stephanopoulus (USA)

Panel U5: Engineering Complex Interfaces for Enhancing Hydrocarbon Recovery with Carbon Storage
Panel Lead: Greeshma Gadikota (USA)

Theme/Focus Area 3: CO_2 storage (S) Don DePaolo (USA), Co-Chair

Panel S1: Injectivity and Capacity – Room 5
Panel Leads: Philip Ringrose (NOR) and Curt Oldenburg (USA)

Panel S2: Monitoring, Verification and Performance Metrics – Room 11
Panel Leads: Ziqiui Xue (JPN) and Jonathan Pearce (UK)

Panel S3: Forecasting and Managing Induced Seismicity – Room 12
Panel Leads: Hideo Aochi (FRA) and David Eaton (CAN)

Panel S4: Well Diagnostics – Room 10
Panel Leads: Franz May (GER) and Rick Chalaturnyk (CAN)

Crosscut (CC) Joe Powell (USA), Co-Chair – Galileo I

Panel Leads: Jay Lee (KOR) and Andrea Ramirez (NLD)

MISSION INNOVATION

Accelerating the Clean Energy Revolution

Carbon Capture Innovation Challenge