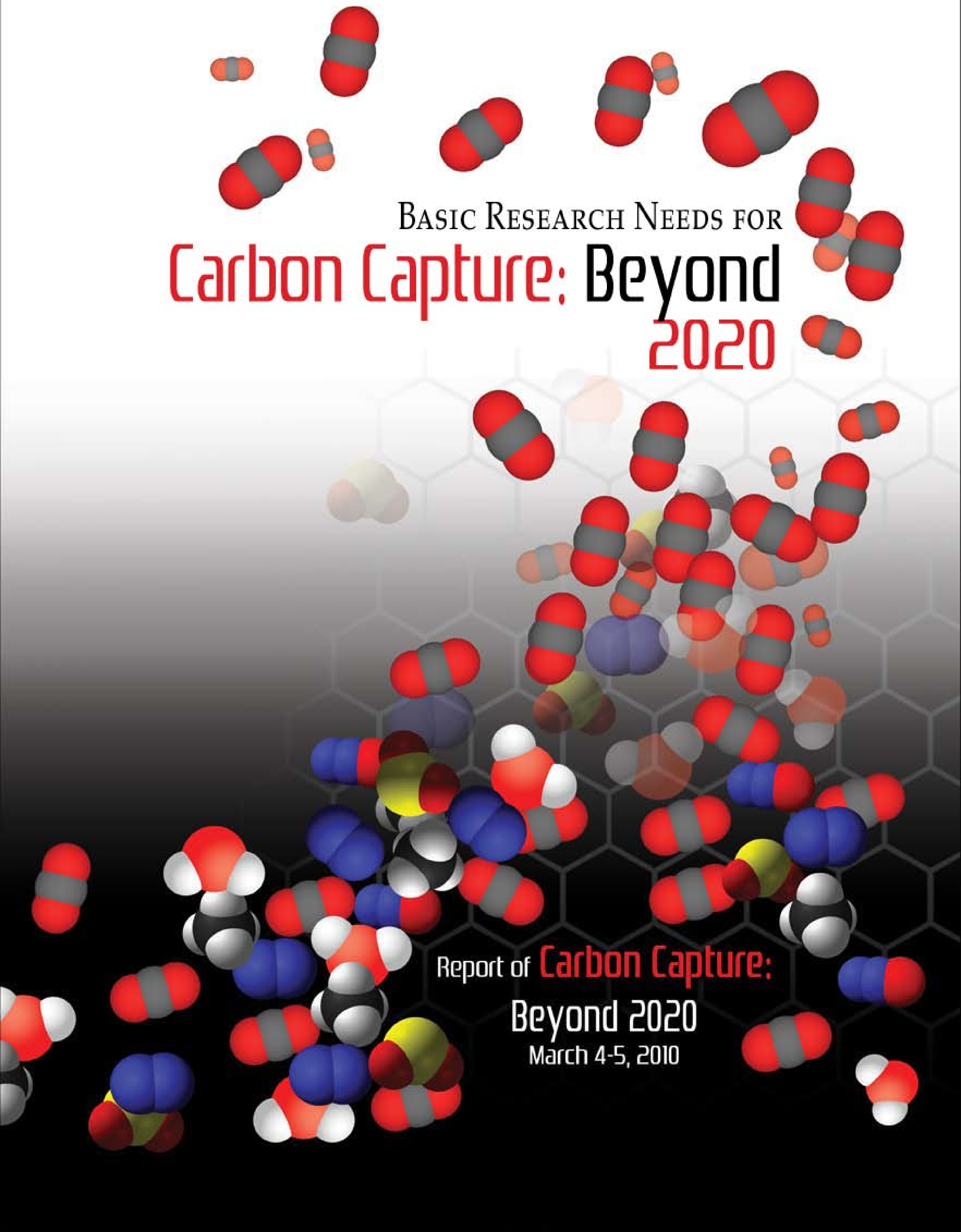

Basic Research Needs for

Carbon Capture: Beyond 2020

Report of Carbon Capture:

Beyond 2020

March 4-5, 2010

The cover illustration depicts carbon dioxide, a gray carbon atom with two red oxygen atoms, being separated from a combustion stream containing a complex mixture of gases, including carbon dioxide, nitrogen (two blue atoms), water (two white hydrogen atoms and one red oxygen atom), methane (four white hydrogen atoms and one black carbon atom), sulfur dioxide (one yellow sulfur atom and two red oxygen atoms), and nitrous oxide (two blue nitrogen atoms and one red oxygen atom).

BASIC RESEARCH NEEDS FOR CARBON CAPTURE: BEYOND 2020

Report of the Basic Energy Sciences Workshop for Carbon Capture: Beyond 2020

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	Membranes Benny Freeman, University of Texas, Austin Samuel Stupp, Northwestern University
	Solid Sorbents Omar Yaghi, University of California, Los Angeles Chris Murray, University of Pennsylvania
	Crosscutting Theory, Modeling, and Simulation Berend Smit, University of California, Berkeley Paulette Clancy, Cornell University
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This report is available on the web at http://www.sc.doe.gov/bes/reports/files/CCB2020_rpt.pdf

CONTENTS

FIGURES

Figure **Page**

ABBREVIATIONS, ACRONYMS, AND INITIALISMS

1D	one-dimensional
2D	two-dimensional
3D	three-dimensional
AMBER	Assisted Model Building with Energy Refinement (public domain force field codes for the simulation of biomolecules)
BES	DOE Office of Basic Energy Sciences
CHARMM	Chemistry at HARvard Macromolecular Mechanics (widely used molecular simulation program)
CNT	carbon nanotube
CO_2	carbon dioxide
COF	covalent organic framework
CT	computerized tomography
DBU	1,8-diazabicyclo(5.4.0)undec-7-ene
DFT	density functional theory
DOE	US Department of Energy
FE	DOE Office of Fossil Energy
Fe_2O_3	hematite
Fe_3O_4	magnetite
FLOPS	floating point operations per second
GPU	graphic processing unit
IR	infrared
Li_2ZrO_3	lithium zirconate
MAS	magic-angle spinning
MC	Monte Carlo
MD	molecular dynamics
MEA	monoethanolamine
MOF	metal-organic framework
NMR	nuclear magnetic resonance
NO_x	gaseous oxides of nitrogen
O_2	oxygen
OPLS	Optimized Potentials for Liquid Simulations (force field codes similar to AMBER)

oxycombustion	production of relatively pure oxygen (O_2) prior to combustion
PDE	partial differential equation
ppm	parts per million
PRD	Priority Research Direction
ROH	alcohol
SFG	sum-frequency spectroscopy
SO_x	gaseous oxides of sulfur
SPM	scanning probe microscopy
STEM	scanning transmission electron microscopy
TraPPE-UA	Transferable Potentials for Phase Equilibria-United Atom (family of force field codes used in biomolecule simulations)
TXM	transmission x-ray microscopy
UNIFAC	UNIversal Functional Activity Coefficient (free-energy prediction model used in molecular dynamics simulations)
UNIQUAC	UNIversal QUAsiChemical (phase equilibrium model used in molecular dynamics simulations)
vdW-DF	van der Waals–density functional
XRD	x-ray diffraction
ZIF	zeolite/zeolitic imidazolate/inorganic framework

EXECUTIVE SUMMARY
OF THE DOE BASIC ENERGY SCIENCES WORKSHOP

BASIC RESEARCH NEEDS FOR CARBON CAPTURE BEYOND 2020

The problem of thermodynamically efficient and scalable carbon capture stands as one of the greatest challenges for modern energy researchers. The vast majority of US and global energy use derives from fossil fuels, the combustion of which results in the emission of carbon dioxide into the atmosphere. These anthropogenic emissions are now altering the climate.[1] Although many alternatives to combustion are being considered, the fact is that combustion will remain a principal component of the global energy system for decades to come. Today's carbon capture technologies are expensive and cumbersome and energy intensive. If scientists could develop practical and cost-effective methods to capture carbon, those methods would at once alter the future of the largest industry in the world and provide a technical solution to one of the most vexing problems facing humanity.

The carbon capture problem is a true grand challenge for today's scientists. Postcombustion CO_2 capture requires major new developments in disciplines spanning fundamental theoretical and experimental physical chemistry, materials design and synthesis, and chemical engineering. To start with, the CO_2 molecule itself is thermodynamically stable and binding to it requires a distortion of the molecule away from its linear and symmetric arrangement. This binding of the gas molecule cannot be too strong, however; the sheer quantity of CO_2 that must be captured ultimately dictates that the capture medium must be recycled over and over. Hence the CO_2 once bound, must be released with relatively little energy input.[2] Further, the CO_2 must be rapidly and selectively pulled out of a mixture that contains many other gaseous components.[3] The related processes of precombustion capture and oxycombustion pose similar challenges. It is this nexus of high-speed capture with high selectivity and minimal energy loss that makes this a true grand challenge problem, far beyond any of today's artificial molecular manipulation technologies, and one whose solution will drive the advancement of molecular science to a new level of sophistication.

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[1] For more than the last 420,000 years, the concentration of CO_2 in the environment has varied between 180 and 280 parts per million (ppm) as the Earth has moved between glacial and interglacial periods, but it has never exceeded 280 ppm.[1] After the beginning of the industrial revolution, however, the concentration of atmospheric CO_2 has steadily climbed, to about 390 ppm in 2010 [http://www.esrl.noaa.gov/gmd/ccgg/trends/]. The emission of CO_2, if left unchecked, is projected to exceed 500 ppm in 2050 as world demand for energy climbs and more coal, oil, and natural gas are consumed. CO_2 in the atmosphere acts a positive forcing on the climate. The best estimates of the sensitivity of the global temperature to a doubling of atmospheric CO_2, including feedbacks, is about 4°C.[2] The complete set of impacts that will result from the increased CO_2 concentrations are not known, but many observations have already correlated changes in temperature, precipitation, sea levels, ocean pH, and other climate-related parameters with these increased concentrations [http://www.ncdc.noaa.gov/oa/climate/globalwarming.html].

[2] Anthropogenic global CO_2 emissions of 30 gigatons a year dwarf by more than a factor of 60 the top 100 bulk commodity chemicals produced.

[3] A typical 550 MW coal-fired electrical plant produces about 2 million ft^3 of flue gas *per minute,* containing a mixture of CO_2, H_2O, N_2, O_2, NO_x, SO_x, and ash. However, the CO_2 is present at very low concentrations (<15%) after conventional combustion, requiring very effective separation processes. Precombustion strategies, in which coal is gasified prior to combustion, can be used to increase the concentration of CO_2 in the flue gas to about 40%. In oxycombustion, purified oxygen (separated from air) is used in the combustion process, resulting in a flue gas that is predominately CO_2 (over 60%) in steam, making separation a matter of cooling to condense steam.

We have only to look to nature, where such chemical separations are performed routinely, to imagine what may be achieved. The hemoglobin molecule transports oxygen in the blood rapidly and selectively and releases it with minimal energy penalty. Despite our improved understanding of how this biological system works, we have yet to engineer a molecular capture system that uses the fundamental cooperativity process that lies at the heart of the functionality of hemoglobin. While such biological examples provide inspiration, we also note that newly developed theoretical and computational capabilities; the synthesis of new molecules, materials, and membranes; and the remarkable advances in characterization techniques enabled by the Department of Energy's measurement facilities all create a favorable environment for a major new basic research push to solve the carbon capture problem within the next decade.

The Department of Energy has established a comprehensive strategy to meet the nation's needs in the carbon capture arena. This framework has been developed following a series of workshops that have engaged all the critical stakeholder communities. The strategy that has emerged is based upon a tiered approach, with Fossil Energy taking the lead in a series of applied research programs that will test and extend our current systems. ARPA-E (Advanced Research Projects Agency–Energy) is supporting potential breakthroughs based upon innovative proposals to rapidly harness today's technical capabilities in ways not previously considered. These needs and plans have been well summarized in the report from a recent workshop—*Carbon Capture 2020,* held in October 5 and 6, 2009—focused on near-term strategies for carbon capture improvements (http://www.netl.doe.gov/publications/proceedings/09/CC2020/pdfs/Richards_Summary.pdf). Yet the fact remains that when the carbon capture problem is looked at closely, we see today's technologies fall far short of making carbon capture an economically viable process. This situation reinforces the need for a parallel, intensive use-inspired basic research effort to address the problem. This was the overwhelming conclusion of a recent workshop—*Carbon Capture: Beyond 2020,* held March 4 and 5, 2010—and is the subject of the present report. To prepare for the second workshop, an in-depth assessment of current technologies for carbon capture was conducted; the result of this study was a factual document, *Technology and Applied R&D Needs for Carbon Capture: Beyond 2020*. This document, which was prepared by experts in current carbon capture processes, also summarized the technological gaps or bottlenecks that limit currently available carbon capture technologies. The report considered the separation processes needed for all three CO_2 emission reduction strategies—postcombustion, precombustion, and oxycombustion—and assessed three primary separation technologies based on liquid absorption, membranes, and solid adsorption.

The workshop "Carbon Capture: Beyond 2020" convened approximately 80 attendees from universities, national laboratories, and industry to assess the basic research needed to address the current technical bottlenecks in carbon capture processes and to identify key research priority directions that will provide the foundations for future carbon capture technologies. The workshop began with a plenary session including speakers who summarized the extent of the carbon capture challenge, the various current approaches, and the limitations of these technologies. Workshop attendees were then given the charge to identify high-priority basic research directions that could provide revolutionary new concepts to form the basis for separation technologies in 2020 and beyond. The participants were divided into three major panels corresponding to different approaches for separating gases to reduce carbon emissions—liquid absorption, solid adsorption, and membrane separations. Two other panels were instructed to attend each of these three technology panels to assess crosscutting issues relevant to characterization and computation. At the end of the workshop, a final plenary session was convened to summarize the most critical research needs identified by the workshop attendees in each of the three major technical panels and from the two cross-cutting panels.

The reports of the three technical panels included a set of high level Priority Research Directions meant to serve as inspiration to researchers in multiple disciplines—materials science, chemistry, biology, computational science, engineering, and others—to address the huge scientific challenges facing this nation and the world as we seek technologies for large-scale carbon capture beyond 2020. These Priority Research Directions were clustered around three main areas, all tightly coupled:

- Understand and control the dynamic atomic-level and molecular-level interactions of the targeted species with the separation media.
- Discover and design new materials that incorporate designed structures and functionalities tuned for optimum separation properties.
- Tailor capture/release processes with alternative driving forces, taking advantage of a new generation of materials.

In each of the technical panels, the participants identified two major crosscutting research themes. The first was the development of new analytical tools that can characterize materials structure and molecular processes across broad spatial and temporal scales and under realistic conditions that mimic those encountered in actual separation processes. Such tools are needed to examine interfaces and thin films at the atomic and molecular levels, achieving an atomic/molecular-scale understanding of gas–host structures, kinetics, and dynamics, and understanding and control of nanoscale synthesis in multiple dimensions. A second major crosscutting theme was the development of new computational tools for theory, modeling, and simulation of separation processes. Computational techniques can be used to elucidate mechanisms responsible for observed separations, predict new desired features for advanced separations materials, and guide future experiments, thus complementing synthesis and characterization efforts. These two crosscut areas underscored the fact that the challenge for future carbon capture technologies will be met only with multidisciplinary teams of scientists and engineers. In addition, it was noted that success in this fundamental research area must be closely coupled with successful applied research to ensure the continuing assessment and maturation of new technologies as they undergo scale-up and deployment.

Carbon capture is a very rich scientific problem, replete with opportunity for basic researchers to advance the frontiers of science as they engage on one of the most important technical challenges of our times. This workshop report outlines an ambitious agenda for addressing the very difficult problem of carbon capture by creating foundational new basic science. This new science will in turn pave the way for many additional advances across a broad range of scientific disciplines and technology sectors.

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INTRODUCTION

INTRODUCTION

Most of the world's energy is based on carbon, including fossil fuels—coal, petroleum, and natural gas—as well as biomass and bio-based fuels. Combustion of carbon and hydrogen in these fuels results in the release of heat (the source of energy), along with gaseous products, water and carbon dioxide (CO_2), and other materials, such as ash. In 2007 global energy use accounted for over 85% of the 37,000,000,000 tons (37 Gt) of CO_2 released to the atmosphere. In the United States, nearly 40% of atmospheric CO_2 can be attributed to combustion of fossil fuels to produce electricity, with another 30% resulting from industrial processes and 30% from transportation. As demands for energy have increased globally, CO_2 levels have risen sharply, from preindustrial levels of 280 ppm a century ago to over 380 ppm in 2009. These levels are projected to increase even more dramatically over the next 50 years as global demands for energy are anticipated to double. The 1992 U.N. Framework Convention on Climate Change called for "stabilization of greenhouse gas concentrations in the atmosphere at a level that would prevent dangerous anthropogenic interference with the climate system." Further, this report stated that a stabilizing goal of $\leq$450 ppm CO_2 is needed to avoid serious impacts to the environment.[1]

Stabilizing atmospheric CO_2 concentrations will require enormous reductions in CO_2 emissions. Alternate energy sources that release no carbon into the atmosphere during use—solar, wind, geothermal, hydro, and nuclear—offer ultimate solutions to curb global CO_2 increases. However, many technologies based on efficient generation of electricity from non-carbon-based energy sources and technologies that use energy produced from these sources, such as plug-in electric or hydrogen-fueled vehicles, are either still in development or in an early stage of commercialization. It will take decades to deploy these zero-carbon technologies at a level that will make a significant impact on reducing fossil fuels as an energy source globally. Thus for the foreseeable future, the world will still depend primarily on the combustion of carbon-based fuels for energy.

Carbon capture combined with sequestration is the only means of reducing CO_2 emissions in the near term and could serve as a bridging strategy to a time when noncarbon energy technologies are broadly deployed. In addition, conversion of CO_2 (e.g., reduction to methane or methanol) could help reduce the amount needing to be sequestered. However, the magnitude of the problem of unfettered carbon emissions to the environment is daunting: continued use of fossil fuel while capping the atmospheric concentration of CO_2 at levels of less than 500 ppm is projected to require the capture of ~10 Gt of CO_2 per year globally—over a quarter of the CO_2 that is generated globally today—and the problem continues to grow as energy use grows.

Large-scale carbon capture is most effective at sites where large quantities of CO_2 are generated, including large electrical energy generating plants fueled by fossil fuels or biomass; major industrial sites (e.g., for cement, steel, or aluminum production or ethanol fermentation); or facilities in which natural gas, petroleum, synthetic fuels, or fossil-based hydrogen is produced. A typical 550 MW coal-fired electrical plant produces about 2 million cubic feet of flue gas per minute at atmospheric pressure. This large volume of postcombustion flue gas contains CO_2 at concentrations of about 12–14% along with water;

nitrogen; oxygen; and traces of sulfur oxides, nitrogen oxides, and other materials originating from the fuel and the air used for combustion. Thus capturing CO_2 from this complex mixture at high levels of purity requires highly efficient separation techniques. In addition to capturing CO_2 after combustion, strategies for reducing CO_2 emissions include precombustion capture and oxycombustion. Precombustion capture is primarily applicable to gasification plants in which the fuel (e.g., coal, biomass) is converted to gaseous components prior to combustion; it concentrates the levels of CO_2 to greater than 40%. In oxycombustion, relatively pure oxygen is used in the combustion process and produces CO_2 at levels of about 60%. The advantage of both of these processes is that CO_2 is produced in significantly higher concentrations than with postcombustion capture processes, making capture much more efficient.

In all three strategies, CO_2 must be efficiently separated from other gaseous components or water vapor for subsequent sequestration or conversion. While CO_2 capture is relatively easy with oxycombustion, the process requires the ability to separate oxygen from air at low cost. Currently, three main types of separation strategies are used—liquid absorbents, solid adsorbents, and membranes—all of which are described in detail later in this report. All three of these separation strategies depend upon materials and chemical and physical processes to separate a targeted gas from a mixture. Although some of today's technologies for capturing CO_2 may be relatively efficient, all require considerable energy for isolation of the $CO_{2.}$ This is because current separation techniques require changes in temperature and/or pressure to drive the separation process. In addition, because of the massive volumes of CO_2 that must be captured, regeneration of the capture materials for reuse is required. This means that a driving force is needed to release the CO_2 after capture. Carbon capture materials currently used, including aqueous amines, require a large amount of energy to release the captured CO_2. The energy required for these separation and release processes lowers the overall efficiency of a power generating facility, resulting in substantially higher overall costs for electricity (as much as 50–80% higher) compared with facilities without carbon capture. To realize the goal of capping environmental concentrations of CO_2 while the demands for energy continue to increase, there is a critical need for next-generation separation concepts that will provide efficient, cost-effective technologies for carbon capture in the future.

The Department of Energy, both the Office of Basic Energy Sciences and Fossil Energy, convened two workshops; the first, Carbon Capture 2020, was held in October 2009, and was led by FE. The current workshop was led by BES and was convened with the recognition that the challenges for efficient carbon capture will not be met by simple incremental improvements in current technologies. The workshop participants were charged with identifying fundamental research needs and opportunities that would provide the underpinning knowledge needed to make the significant advances in separation technologies required for carbon capture. Prior to the workshop, industry and applied research laboratories prepared a technology resource document, *Technology and Applied R&D Needs for Carbon Capture: Beyond 2020* (Appendix A of this report), which provided the foundation on which the workshop participants initiated discussion at the workshop. The workshop was attended by more than 70 scientists from universities, national laboratories, and industry, as well as representatives from the Department of Energy (DOE) Office of Basic Energy Sciences, the DOE Office of Fossil Energy, and the Advanced Research Projects Agency–Energy.

The workshop was opened by William Brinkman, Director, DOE Office of Science, and Victor Der, Principal Deputy Assistant Secretary for the DOE Office of Fossil Energy. Three plenary speakers provided additional insight on the challenges of carbon capture: Edward Rubin (Carnegie Mellon Institute), "Challenges and Opportunities for Advanced Carbon Capture," Abhoyjit Bhown (Electric Power Research Institute), "Status of Post-Combustion CO_2 Capture Technologies," and Rodney Allam (NET Power, LLC), "Carbon Dioxide Capture Using Oxy-Fuel Systems." The workshop participants also found inspiration from two important observations. First, it was noted that efficient chemical and physical processes are readily found in nature to separate CO_2 and O_2 in air and liquids, forming the basis of respiration in plants and animals. Second, the participants recognized that recent advances in the design of materials and in chemical processes at the nanoscale have provided surprising new functionalities never before thought possible. Based on all of this background information, the workshop participants evaluated technology bottlenecks in existing carbon capture processes and identified high-priority fundamental research directions for realizing wholly new approaches to reduce carbon emissions efficiently.

Three technology panels were formed to assess three major separations methods—Membranes, Liquid Absorption, and Solid Adsorption—and these three areas form the foundation of this report. Each panel prepared a report that outlines the major challenges for each technology area. In addition to the three technology panels, two additional panels were convened that identified issues that were common to all three technology panels. These two crosscut panels focused on new analytical and computational tools that will be needed to support research activities focused on identifying, predicting, and understanding atomic-level and molecular-level processes that are critical for separation technologies. All five panels then identified the most promising fundamental research areas that could result in revolutionary, rather than just incremental, advances in separation. These Priority Research Directions (PRDs) are designed to inspire multidisciplinary teams of scientists and engineers to develop a new understanding of chemical and physical interactions at the interfaces of gases, liquids, and solids that could provide entirely new paradigms for separating CO_2, O_2, and other gases efficiently and cost effectively. This knowledge will form the basis for designing revolutionary strategies for reducing the emission of CO_2 in the future. These strategies will include new materials and new chemical and physical processes that take advantage of molecular-level interactions that can be altered by drivers other than temperature and pressure to isolate and then release CO_2 quickly and reversibly. The result will be the design of highly efficient and cost-effective separation systems that will mitigate a serious two-pronged dilemma confronting the world: increased production of CO_2 globally as energy demand substantially increases and the concomitant deleterious impacts of climate change.

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BASIC RESEARCH NEEDS FOR CARBON CAPTURE

LIQUID ABSORBENTS

Current Status

The connection between the amount of gas dissolved in a liquid and pressure is familiar to anyone who has ever opened a bottle or can of soda pop (Figure 1). At the relatively high pressure of the unopened bottle, CO_2 gas is mostly dissolved into the soda. Opening the bottle reduces the pressure, decreases the solubility, and produces the satisfying pop and fizz of escaping CO_2. Fortunately for soda drinkers, under normal conditions all the dissolved CO_2 doesn't escape instantly—bubbles continue to emerge slowly until the soda goes "flat." The cooler the soda, the more gas that remains dissolved, and the more refreshing the soda!

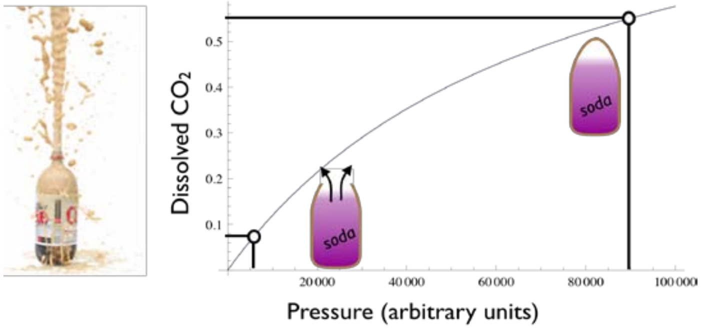


Figure 1. Releasing the pressure on a bottle of soda pop causes dissolved CO_2 to leave the liquid—slowly under normal conditions, or spectacularly if the transfer is promoted with an appropriate accelerating additive.[1] This effect is due to the fundamental relation between pressure and dissolved gas, as captured in an isotherm (right).

Absorbent-based gas separations play on the same processes occurring in the soda bottle. The solubility of a gas in a liquid as a function of pressure is described by an isotherm like that shown in Figure 1. "Opening the bottle" reduces the pressure and moves the mixture from a high to low solubility point. These isotherm shapes depend on other factors as well, such as temperature, and these differences can be exploited to separate a gas mixture. Figure 2 illustrates this process for a *temperature-swing* separation in which changes in solubility with temperature are used to effect separation of a target component from a mixture. In this example, CO_2 selectively dissolves to a high concentration from a mixture of gases into the cool absorbent, separating it from the other gases (the "diluents"), which are rejected. The CO_2-saturated liquid absorbent is moved to a stripper and its temperature is raised, lowering the CO_2 solubility and releasing a gaseous stream of pure CO_2. The CO_2-depleted absorbent is then cooled to restart the cycle.

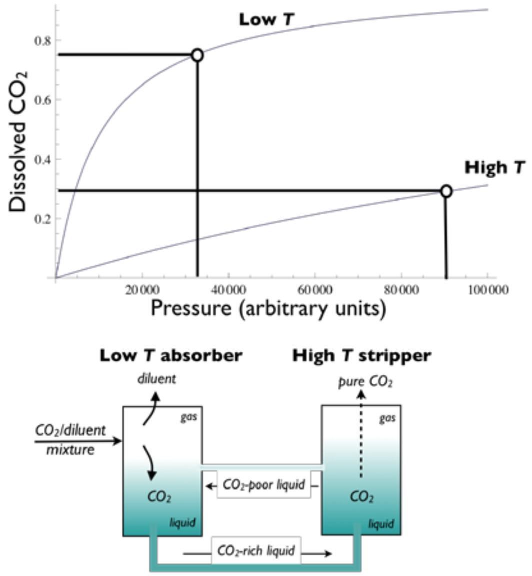


Figure 2. Absorption gas separation using temperature-swing gas separation takes advantage of the high solubility of target gas at low temperature and lower solubility at high temperature.

As suggested from this example, separating a mixture of gases into its constituents takes energy—in fact it is a fundamental consequence of thermodynamics that this energy cost can never be completely avoided. But it can be altered by changing the boundaries or shapes of these isotherms, changing how they vary with temperature or other factors and changing the selectively with which the liquid combines with the gas of interest. One of the fundamental scientific challenges of liquid adsorption is to control the solubility of the gas in the liquid in a way that minimizes the energy cost of a desired separation.

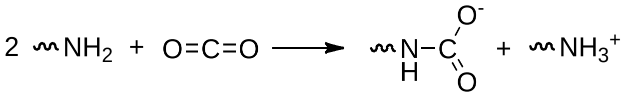
As described earlier, all the CO_2 does not instantly escape from the soda when the bottle is opened. Rather, it takes time for the transfer from liquid to gas to happen, and time is another key factor in using absorbents for gas separation. The soda drinker is generally happy for the CO_2 to stay in the soda; the gas separations engineer generally is not. The time to transfer to and from the liquid and gas phases is determined by the rates of mass transfer, which ultimately depend on the microscopic processes that move molecules from one place to another. Slow rates imply slow processes that translate, ultimately, into larger, more costly separation systems. In the case of CO_2 in H_2O, the rates of these processes are intrinsically too slow to be practically useful for gas separations, and other materials, such as catalysts, must be used to speed the transfer. This is the effect illustrated so dramatically in Figure 1.[1]

Liquid absorbents have many practical advantages for the large-scale gas separations necessary for practical carbon capture and sequestration: liquids are easy to handle and to pump around in large quantities; technologies are well developed for heating and cooling liquids and for contacting liquids with gases in separations processes; and liquids can exhibit high gas solubility and selectivity. In addition, there is a wealth of experience in employing liquid absorbents in industrial processes.

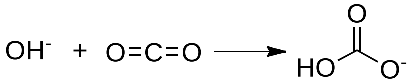
Absorbents can exhibit a wide range of affinities for a gas molecule.

- Physical, nonreacting absorbents effect separations using weak interactions between the target gas and absorbent. This approach is most useful when separating gases across a large pressure difference or when the concentration of target gas is high.
- Reactive absorbents (chemical absorbents) effect separations using some type of chemical reaction between the target gas and the absorbent. This approach is useful for situations with smaller pressure differences, which require larger binding energies.

Physical solvents are used in many “gas-sweetening” applications in which acidic gases, like SO_2 and CO_2, are removed from a gas stream. These separations take advantage of various types of organic solvents, such as glycols.[2] They are also appropriate for precombustion CO_2 removal. CO_2 has been separated from natural gas for many years using chemical absorption. As discussed in the sidebar “Aqueous Amines for CO_2 Separation,” aqueous amines are commonly used to perform this separation: the amines combine strongly and selectively with CO_2, the solubilization process is relatively fast, and the amines themselves are inexpensive.[3] Mechanisms depend on the particulars of the amine but are generally thought to involve some combination of carbamate and bicarbonate formation, depending on the amine basicity and number of substituents:



$$2\ {\sim}NH_2 + O{=}C{=}O \longrightarrow {\sim}\underset{H}{N}{-}C(=O)O^- + {\sim}NH_3^+$$

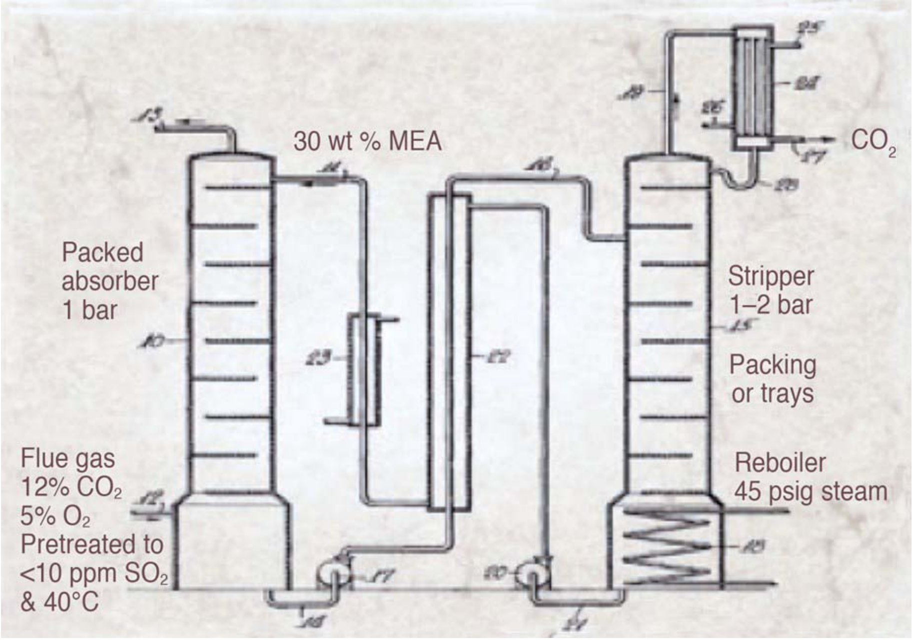


Although various classes of amines have been explored, including chilled ammonia itself, improvements in the ability to separate CO_2 by this approach have been incremental. Further, these separations are primarily driven by temperature swing (i.e., absorption at low temperature, desorption at high temperature), a reliable but not necessarily optimally efficient means. Nonetheless, these relatively mature methods are the ones most commonly discussed and most actively developed for use in postcombustion carbon capture.

Aqueous Amines for CO_2 Separation

The capture of CO_2 by aqueous amines has been practiced for over 80 years[3] in the removal of CO_2 from natural gas and hydrogen and in producing beverage-grade CO_2. In a typical process, flue gas that contains CO_2 is contacted with an aqueous amine solvent in an absorber column at a relatively low temperature and is absorbed. The loaded solvent is pumped to a stripping column where it is heated to regenerate the solvent and release the CO_2. The hot regenerated solvent is then returned to the absorber column through a heat exchanger, which cools the hot solvent and preheats the rich solvent going to the stripper. Most of the energy required to capture CO_2 is consumed in heating the rich solvent in the stripper column.

It is essential to consider the entire CO_2 capture process when evaluating the efficiency and energy cost of capture. For example, developing a solvent with a low absorption energy for a thermal swing regeneration may not result in an energy savings because of the need for additional heat to maintain pressure, or the need for additional compressors downstream of the absorber to obtain sequestration pipeline pressures.[4] Alternatively, the low absorption energy solvent may work more efficiently in a vacuum desorption process.[5]



The original patented process for aqueous amine solvent scrubbing.[3]

These current CO_2 capture methods also have other limitations. Water and amines are themselves volatile, contributing to the energy costs of the separation and resulting in the loss of absorbent over time. Certain contaminants, such as the sulfur oxides, interfere with the amine–CO_2 reaction. The amine absorbents themselves are corrosive and also decompose over time. Most important, a high amount of energy is required to drive these separations, representing a significant fraction of the energy produced by combusting coal.

Other industrial applications of liquid absorbents to separate other gases are far less common. The separation of oxygen (O_2) from air, needed to enable oxyfuel combustion, is in fact performed very effectively in the body. Blood is a complex, hierarchically structured liquid that builds on components (hemoglobin) tailored from the molecular level to selectively bind O_2 and transport it to cells. In these cells, the oxygen is used in the biological analog of oxyfuel combustion. We have not yet learned to master these approaches in the way nature has, but this powerful example illustrates the potential for expanding liquid absorption into broader domains that could revolutionize the ability to separate targeted gases from air.

Basic Science Challenges and Opportunities

The properties of an ideal gas-separating liquid absorbent are clear:

- It should have a high *selectivity* toward binding the gas of interest over all the other gases in the mixture to be separated.
- It should have a high *capacity* to bind the gas at one condition.
- It should readily *release the gas on demand* with a minimal amount of input energy at another desired condition.
- It should support *fast and reversible* transport and reaction between gas and absorbent phases.
- It should be *thermally and chemically stable* in the environment of intended use.
- It should have *physical properties* (e.g., heat capacity, density, viscosity, vapor pressure, enthalpy of vaporization) that are well matched to use.
- It should be *readily synthesized* from abundant and accessible precursors.

Today’s inventory of liquid absorbents for carbon capture and other applications are far from this absorbent paradise. Rather than having control over these properties and characteristics to effect selective separations, we are currently constrained to make do with the properties of known classes of materials and to design separation systems to accommodate the properties. Our toolkits for tuning the chemical and physical properties of absorbents are limited and largely empirical; consequently, the pool of approaches available for driving separations is equally limited.

The enticing opportunity is to invert this practice, so that rather than the separation process and conditions being fitted to the available absorbents, the absorbent properties are tailored to be optimally suited to the desired separation. There are several basic scientific challenges that must be overcome to realize the full potential of liquid absorbents for separation of targeted gases:

- The basic physical processes at work in the absorbent bulk and at the critical absorbent–gas interface must be understood and modeled in detail. Absorbents must be characterized in the working state, at spatial and temporal resolutions commensurate with separation processes. We need to answer basic questions about the liquid-gas system: What effect does dissolved gas have on the structure and properties of a liquid in the bulk and at the interface? What mechanisms, at the molecular level, are available to control selectivity toward one gas over another? What mechanisms govern the rates of gas transport and accommodation into (or out of) a liquid? How do we measure these properties, and how do we describe them in sufficient detail to guide the design of separation systems? (See the sidebar "Interfacial Reactions.")

- Governing structure–property relations must be understood at a sufficient level of chemical and physical detail to enable rational absorbent material design. How do we go from basic molecular-level understanding to predictive models of physical and chemical absorbent properties? How do we design new absorbents based on this knowledge?
- The toolkit of approaches for driving separations must be radically expanded to encompass new chemistries, new classes of materials, and new physical and chemical switches that go beyond the traditional thermal and pressure swings. How can chemistry (and biochemistry) be exploited to efficiently and selectively separate one gas from others? What sorts of triggers can we use to turn the absorption of a gas either on or off? Can these triggers take advantage of otherwise wasted energy, or alternative energy sources, such as solar?
- Approaches must be developed to synthesize absorbent materials quickly at the lab scale and economically at the very large scales necessary for carbon capture. How can the discovery of new chemistries and preparation of new compounds be accelerated? How can highly selective, functional materials be prepared from abundant resources?
- New computational methods are needed to enable the rational design of new absorbents and to understand, at the molecular level, the physical and chemical processes that are critical to highly selective and efficient separations. How can computation at all levels be leveraged to accelerate discovery?

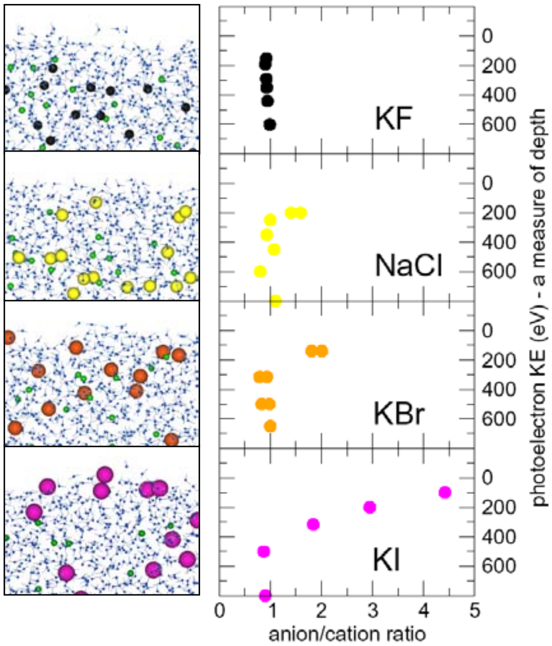
Real-world separations, such as the separation of CO_2 from combustion streams or O_2 from air, are invariably complex, multivariate problems; and one absorbent will never be uniquely and universally optimal. Rather, an additional opportunity is to develop methods that produce virtual suites of absorbents, to fundamentally interconnect the optimization of material and application.

The need for new approaches to CO_2 separation compounds has been recognized in the last several years and has resulted in the discovery of several tantalizing new approaches, such as task-specific ionic liquids,[6,7] "switchable" solvents (see the sidebar "Switchable Solvents"),[8] and "frustrated" acid-base pairs.[9] These discoveries have been largely ad hoc and have yet to make a serious dent in the overall problem. They indicate, though, the potential for revolutionary new advances given sufficient resources and concerted scientific effort.

Conclusion

Liquids-based absorption separation is a proven approach that, with properly tailored absorbents, has the potential to achieve outstanding efficiencies in gas separation in general and postcombustion and oxyfuel separation in particular. The challenges to realizing breakthrough increases are substantial, but the scientific tools are now in place to advance the field from incremental improvements based on limited understanding to true knowledge and insight-driven discovery and optimization.

Interfacial Reactions

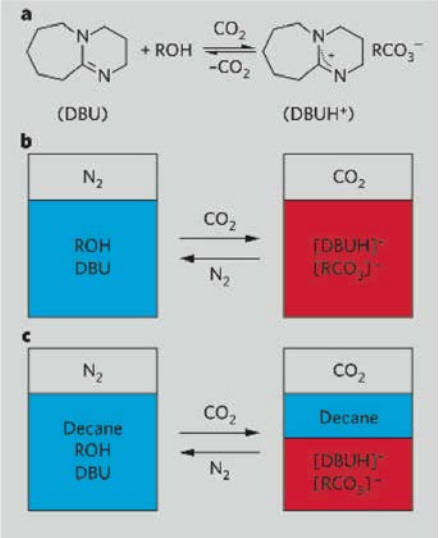


Gas–liquid interfaces. Left panel: Snapshots from molecular dynamics simulations depicting air-solution interfaces of aqueous alkali halide solutions. Right panel: Depth profiles of the anion/cation ratios from photoelectron spectroscopy experiments on deliquesced potassium halide crystals. The prediction of the presence of ions at the air–water interface defied conventional wisdom and stimulated the development of new experiments. The increasing enhancement of the population of the anion over the cation with increasing halide mass predicted by the simulations is verified by the experiment.

Gas–liquid interfaces are tumultuous places, with molecules in the interfacial region involved in a tug-of-war between attractive solvation forces that pull them into the liquid and entropic forces that drive them out. This conflict results in ceaseless, rapid excursions of individual molecules back and forth across the imaginary line separating the two phases. Understanding these complex, dynamic interfaces requires new analytical techniques with the ability to discriminate between molecules in the interfacial region, typically a few molecules thick at most, and those in the vastly larger bulk liquid region. New nonlinear spectroscopies (second harmonic generation and sum frequency generation) are capable of identifying particular species in the interfacial region, but they do not provide depth resolution. Photoelectron spectroscopy, especially with synchrotron light sources, has allowed species-selective depth profiling of a wide range of atomic and molecular species at gas–liquid interfaces. Complementing experimental techniques, molecular dynamics simulations, based on either empirical force fields or ab initio potentials, can provide a dynamic, molecular-scale view of gas–liquid interfaces. Computational methods assist in interpreting experimental data and inspire the development of new experimental capabilities. In turn, modern experiments are providing a wealth of data that can be used to scrutinize and refine theoretical models.[10]

“Switchable” Solvents

Many types of solvents are available to the chemist—polar or nonpolar, aqueous, protic or aprotic, conventional or ionic. Choosing a solvent is often a compromise among the many jobs the solvent must do. But what if the properties of a solvent could be switched from one type to another? Such a switch could be used, for instance, to facilitate the separation of one compound from another. Such switchable solvents have in fact been demonstrated. As shown in the figure, an organic solvent mixture of an amine (DBU) and an alcohol (ROH) can actually be “switched” to an ionic liquid with completely different physical and chemical properties simply by adding CO_2 to the mixture.[8,11] Removing the CO_2 “switches” the solvent back to its original state. In the example shown, this switch is used to separate another organic compound, decaline, from the solvent—decaline is completely soluble in the unswitched state but insoluble in the switched, ionic liquid state.



CO_2 switches a solvent between nonionic and ionic states.[11]

The fact that CO_2 is the chemical switch in this example suggests that this system itself may be useful for CO_2 separations.[12] Even more exciting, though, are the prospects for discovering other solvents and switches designed specifically for CO_2 capture or air separation.

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SOLID SORBENTS

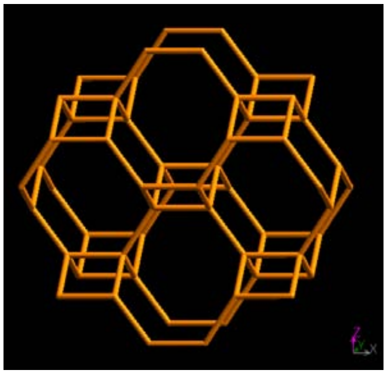
Current Status

When a gas makes contact with a solid, it can be taken up by the solid, just as gaseous odors in your refrigerator can be taken up by activated charcoal or baking soda. The gas either enters the solid (absorption) or remains adhering to the surface of the solid (adsorption). The processes of adsorption and absorption by a solid are collectively referred to as “sorption.” The solid that takes up the gas is the adsorbent, and the gas adhering to the surface is called the adsorbate. It is not easy to distinguish whether the gas is adsorbed or absorbed because most solid materials have pores into which gases can diffuse, and there is not a common technique that could be used to distinguish the two processes if they are occurring simultaneously. However, note that because adsorption requires a gas molecule to make stronger contact with a surface than with itself, the process of adsorption brings gas molecules closer to each other on the surface than off the surface. The gas molecules make contact with the surface through *physisorption* (weak binding to the surface through polarizing forces) or *chemisorption* (strong binding to the surface through strong covalent bonds). Sorption is more energetically favorable than compacting gases by applying high pressure or low temperature.

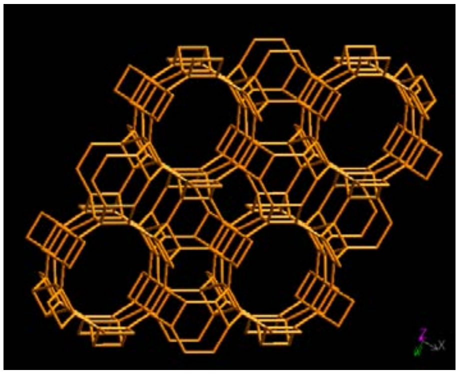
Sorbent materials have a number of design criteria. First, it is preferable to design surfaces that minimize the energy required to remove the adsorbed gas from the surface (i.e., physisorption requires lower energy to release the gas than chemisorption). The increased energy required to release the gas can contribute substantially to the cost of electricity, for example. Second, the gas capture material should have high capacity, meaning that it should possess a large number of surface adsorption sites to which gases may bind. Thus the design of materials with high surface areas is important. High surface area may be achieved either by making small particles of adsorbents or by making materials with highly porous internal structures. Examples of such porous solids include zeolites and activated carbon (see the sidebar “Zeolites and Activated Carbon”), which have surface areas ranging from few hundred m^2/g to over 3,000 m^2/g. Finely divided particles would need to be ~3 nm in size in order to achieve the same level of surface area. These are difficult to make, and their potential adsorbing surfaces are difficult to access because such small particles can pack closely and prevent efficient gas flow. The porous solids overcome this problem because their permanently open structures allow gases to pass through the pores and subsequently bind to their internal surfaces. A third key requirement for solid sorbents is to design the material to allow selective removal of a target gas molecule from mixtures. This selectivity allows the pores to be filled preferentially with one gas, which is subsequently released, allowing the porous material to be reused. The selective binding of a specific gas molecule is accomplished in a porous material by matching the pore openings with the shape and/or size of that gas molecule (shape- and size-selective binding, as shown in Figure 3. Additionally, it is possible to design the steric, electronic, and chemical properties of the adsorption sites within the pores to make the material more selective of specific gas molecules. The advent of nanoscience and the associated synthetic, analytical, and computational capabilities developed to design, synthesize, and characterize materials with specific functionality has the potential to enable a new generation of solid sorbents.

Zeolites and Activated Carbon

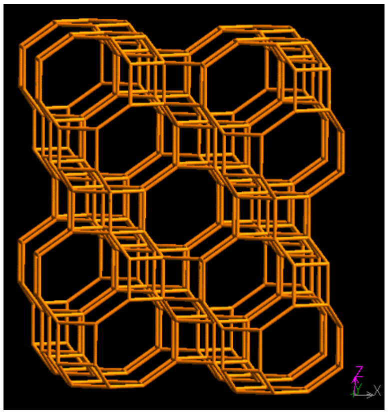
Solid sorbents are commonly found in nature and have been used for years to purify gases and liquids. Activated carbon, also called activated charcoal, is a form of carbon that has been processed to make it extremely porous, yielding a very large surface area available for adsorption. Activated carbon is widely used to purify gases, remove impurities from drinking water, filter impurities from aquarium systems, and even absorb poisons from digestive systems in medical applications. Zeolites, also found in nature, are crystalline aluminosilicates with porous structures. Synthetic versions of these materials have been made with oxide structures containing elements other than aluminum and silicon; however, all zeolites have well-defined pore structures. The metal atoms in zeolites are surrounded by four oxygens in a tetrahedron geometry. The crystalline materials stack into regular arrays, forming channels that permit gas permeation. Depending upon the atoms and structures used in these materials, the sizes and shapes of these channels can be tuned to specific dimensions and can permit selective passage of different gases, like a virtual "molecular sieve." To date, thousands of zeolites have been reported based on hundreds of structures. Three types of structures are shown below that illustrate the channels that can form in these materials. (For more information, see International Zeolite Association Structure Commission, http://www.iza-structure.org/.)



ABW



MAZ



CHA

Zeolite structures. The ABW, MAZ, and CHA structures are three of thousands catalogued by the Structure Commission of the International Zeolite Association in an Internet database of zeolite structures. The commission assigned three-letter framework type codes to all unique, confirmed framework topologies. *Source*: www.iza-structure.org

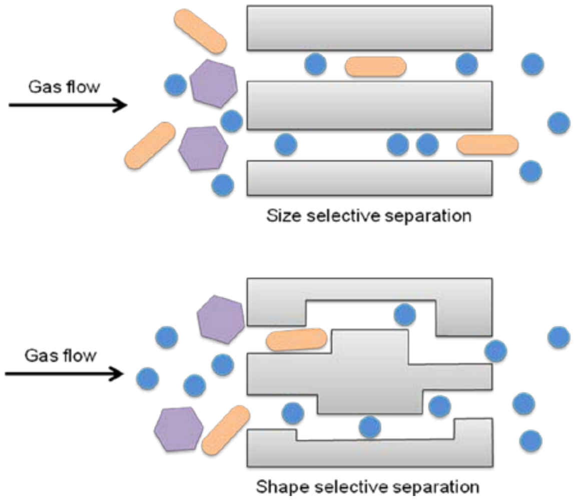


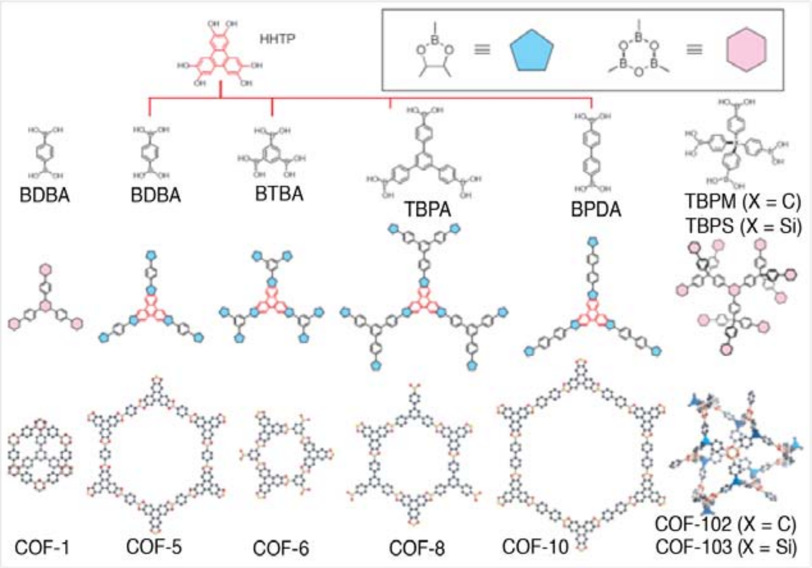
Figure 3. The adsorbent material can be designed to be highly size- and shape-selective.

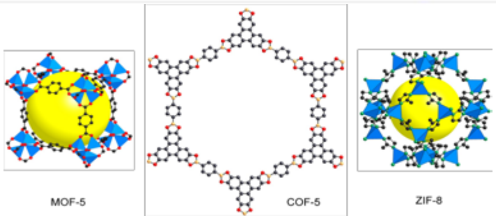
Most solid porous sorbent materials have 3D architectures (see the sidebar "Porous Chemical Architectures") that increase the surface area available for sorption and thereby increase the capacity of the material. To ensure facile kinetics for uptake and release of CO_2, solid sorbents can be designed to have very large surface-to-volume ratios. Most such materials are made up of porous solids or high-surface-area particulates, such as activated carbon,[1] zeolites, and other porous silica-based materials.[2] The primary mode of CO_2 uptake is physisorption, resulting from interactions between the gas and the material. The current limitations of these types of solid adsorbents for gas sorption include low capacity of CO_2 uptake in porous carbons and the energy required for removal of CO_2 from zeolites.

There is enormous potential for making solid materials highly selective for the adsorption of targeted gases by modifying the surfaces with specific materials or functional groups.[3] For example, activated carbon materials can be enriched with elements that could result in improved properties. This includes substituting nitrogen for some carbon atoms or impregnating the material with metal ions. These "extra-framework" atoms and metal ions can serve as specific sites for selective adsorption of CO_2.[4] Further, when the interior pores of activated carbons, zeolites, or mesoporous silicates are functionalized with amines, they can reversibly form surface-tethered carbamates upon exposure to induce chemisorption and increase the uptake efficiency at low partial pressures of CO_2.[5–7] A similar approach can be applied to the surfaces of small solid particles, providing a high-surface-area amine-functionalized solid support. While these initial studies with surface modifications show considerable promise, a molecular understanding of the interaction of targeted gases with these functional groups is critically needed to design new sorbents with higher selectivity. This knowledge will also help explain the role of moisture content in the uptake and release efficiency as these new materials are used in real applications.[8] One can imagine developing solid sorbents that would incorporate functionalities that mimic the mechanism nature uses to isolate CO_2 from air. Such mechanisms are found in conversion of CO_2 to sugars in plant photosynthesis and expulsion of CO_2 in respiration in animals. Further, it may also be possible to incorporate active materials into solid sorbents that could introduce entirely new modes of capturing and releasing CO_2. For example, it might be feasible to introduce functionalities that can respond to magnetic fields or radio frequency radiation to facilitate concentration/release of the CO_2. Incorporating a material that exhibits a phase transformation near the temperature of separation could allow the exothermic energy of CO_2 uptake to be adsorbed and later recovered to aid in CO_2 release.

Recently, a new class of materials has been discovered that have considerable potential as solid sorbents, including metal-organic frameworks (MOFs) and zeolitic imidazolate frameworks (ZIFs) (see "Porous Chemical Architectures"). These novel crystals and network

Porous Chemical Architectures





Black, yellow, red, and green spheres represent C, B, O, and N atoms, respectively.
On lower figures, each of the corners is an oxygen-centered Zn_4 tetrahedron bridged by six carboxylates of an organic linker. The large yellow spheres represent the largest sphere that would fit in the cavities without touching the van der Waals atoms of the frameworks. Hydrogen atoms have been omitted.[9]

Recently, new classes of molecularly designed crystalline porous solids have emerged as favorable candidates for gas separation and storage. These are MOFs, ZIFs, and covalent organic frameworks (COFs). MOFs are constructed from transition metal-oxide “joints” linked by organic “struts.” Typically, they are made in polar solutions by mixing a metal salt with an organic carboxylic acid to form insoluble crystalline solids of extended structures. ZIFs are a subclass of MOFs but have structures related to those of zeolites: the transition metal ions (Zn or Co) are bridged by an imidazolate-type link in the same way that the silicon atoms are bridged by an oxide in zeolites. Thus ZIFs are based on the tetrahedral structures of ZIFs. COFs are also crystalline porous solids, but they are entirely composed of light elements (H, B, C, O, N) and linked by strong covalent bonds into 3D porous architectures. MOFs, ZIFs, and COFs have expanded greatly the number of porous materials because of the flexibility with which their components can be varied and functionalized with organic units to make them suitable for gas separation applications.

The advantage of using such porous chemical architectures for gas separations is the access to a large number of internal surface sites, as indicated by their high surface areas (zeolites, 500–900; silicas, ~1,000; porous carbon, 500–1,500; and MOFs, ZIFs, and COFs, 1,000–6,000 m^2/g). The surface area is roughly proportional to the number of surface sites onto which gas molecules can bind, giving these materials very high capacity for storage of gases. The openness of the structures, especially the more recent ones, is immensely useful for fast kinetics in the uptake of gases and the removal of bound gases.

solids combine well-defined coordination environments surrounding metal centers with bridging organic ligands. The wide range of metals and ligands that can be incorporated in these structures can yield an enormous variety of porous structures.[10] The MOFs and ZIFs can separate targeted gases by physisorption or by chemisorption. For example, in a MOF it is possible to bind CO_2 in one of at least three ways, which provide progressively stronger binding energy and therefore require more heat to remove the CO_2: (1) physisorption onto the internal surface, (2) adsorption onto open metal sites within the backbone of the MOF structure where CO_2 binds directly to the metal centers through the oxygen atom, and (3) functionalizing the organic links with amine groups that bind CO_2 by chemisorption through the formation of carbamates.[11,12] For the latter approach, an energy penalty is associated with the desorption of the CO_2, similar to that observed in aqueous amine solutions. Nevertheless, solid sorbents could offer significant advantages over conventional amine-based liquid stripping techniques if the net energy for uptake and release could be optimized and the materials were sufficiently stable upon cycling.[13,14] For example, grafting the amine functionalities onto the solids eliminates the energy penalty associated with heating the water, although breaking the covalent bonds between CO_2 and the amine groups still requires significant energy.[15,16] This problem would be solved if CO_2 release could be coupled to an exothermic structural transformation of the MOF or ZIF framework that would compensate for the endothermic CO_2 desorption. Here, the use of flexible MOFs, whose structures expand and contract upon CO_2 binding and release, may provide an overall thermoneutral process. Because of the large number of possible compositions and structures, there is considerable research potential in the exploration of MOF and ZIF structures and in their evaluation with respect to CO_2 uptake and release.

There have been recent reports of nonporous sorbents demonstrating improved gas sorption and release. Although the thermochemical behavior of zirconates was studied much earlier,[1] the relevence of these systems for high-temperature CO_2 capture was only recently appreciated.[2] Lithium zirconate (Li_2ZrO_3) is a particularly promising candidate for CO_2 separation at the high temperatures experienced in a precombustion type of reactor.[3,4] Although it has been shown that pure Li_2ZrO_3 absorbs a large quantity of CO_2 at high temperatures with a relatively slow sorption rate, addition of potassium carbonate and lithium carbonate was observed to improve the CO_2 sorption rate.[5] In addition to the compositional tuning and exploration of additives, the strategy of grain size engineering appears to provide significant benefits. For example, nanocrystalline zirconates offer markedly enhanced kinetics[6] and point to improvements in total capacity with increased surface adsorption. Understanding the effects of physical and chemical phenomena at the nanoscale may provide important new opportunities to design materials with the composition and grain size for carbon capture applications.

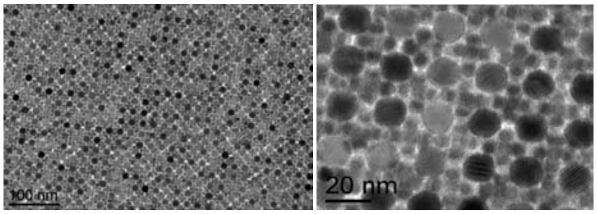


Figure 4. Model nanoporous oxygen carriers.

Figure 4 displays a model oxygen carrier assembled from two complementary sizes of iron oxide particles that can cycle reversibly between hematite (Fe_2O_3 and magnetite (Fe_3O_4). On the left is the result of the reducing cycle, which in the panel on the right has been oxidized on exposure to air. This sample was prepared with a predominantly Fe_2O_3 stoichiometery and was reduced at 500°C in an anaerobic environment while in contact with oleic acid. The organic is consumed, leaving an all inorganic nanoporous network of Fe_3O_4. Exposure to air at ~300°C rapidly effects recovery of the Fe_2O_3 nanostructure. Although the monodisperse 7 and 15 nm grains in the model systems greatly aid imaging and modeling of the process, control of particle size in real world applications is likely to be useful for optimization of surface area and of the interconnected nature of the internal grain boundaries and pores to maximize the rate of oxygen uptake and release. An area of potential interest in new oxygen carrier design is the greater compliance of nanosize grain that may aid in oxygen uptake/release and facilitate ionic transport in the body of the grains.

Basic Science Challenges and Opportunities

Solid sorbents have a huge potential for selective uptake and release of targeted gases in connection with reducing CO_2 emissions in or eliminating them from the atmosphere, whether precombustion or postcombustion. For this potential to be realized, some key fundamental needs have been identified:

- Development of new and improved materials with novel architectures and functionalities that will optimize the selective uptake and release of a targeted gas. This would include development of materials with tailored 3D architectures and appropriate functional groups that facilitate the reversible absorption of target gases.
- A better understanding of the key structural features associated with the efficient, selective sorption of CO_2. This could be approached both theoretically, through molecular modeling, and empirically, through structure/properties relationships studies in solid sorbents.
- Development of new characterization techniques that allow in situ monitoring of gas sorption and real-time analysis of accompanying structural transformations in the sorbent material.
- Identification of new triggers for selective capture and release of gases that drastically reduce the current energy penalties. Nearly 35% of the energy generated in a coal-fired plant can be consumed by carbon capture technologies. So-called smart materials could provide new means of binding and releasing targeted gases without high energy costs.
- Exploration of cooperative phenomena for low-net-enthalpy of cycling. CO_2 absorption/desorption could be coupled with a structural transition in the sorbent so that the overall process is more thermoneutral, alleviating the huge energetic penalty associated with the stripping.

Successfully addressing these scientific challenges requires advanced control over the structure and dynamics of the sorbent materials. Although we have witnessed significant recent progress along this direction, we still know little about designing complexity in a controlled fashion on the atomic and nano scales, and our understanding regarding what makes a sorbent a good carbon capture material remains rudimentary. The magnitude of these challenges calls for a collective research effort that combines new theoretical methods with advances in materials synthesis and characterization, as well as thermodynamic and kinetic studies of gas sorption.

Conclusion

Solid sorbents offer a potential solution to the carbon capture problem, as they are extremely promising materials for efficient, selective sorption of CO_2 and other relevant gases. Although the sorbent materials developed to date are usable, they need further significant improvements to become practical. Incremental modification of the current materials is unlikely to provide a solution. Instead, a whole new generation of materials is needed whose structures and dynamics can be precisely controlled across multiple length scales, from the atomic level to macroscale. The development of such advanced structures will require significant advances in materials modeling, synthesis, and characterization, as well as a detailed understanding of the structure–properties relationships in materials.

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MEMBRANES

Abstract

Three-dimensional architectures are one of the critical structural features of current membrane technologies; however, advancements in the methods to produce such structures have lagged behind the advancements in materials chemistry that have led to dramatic improvements in membrane performance. Recent developments in top-down and bottom-up methods for the production of 3-D architectures provide exciting opportunities to prepare high-performance robust membranes. Such hierarchical structures may offer novel low-energy routes to carbon capture.

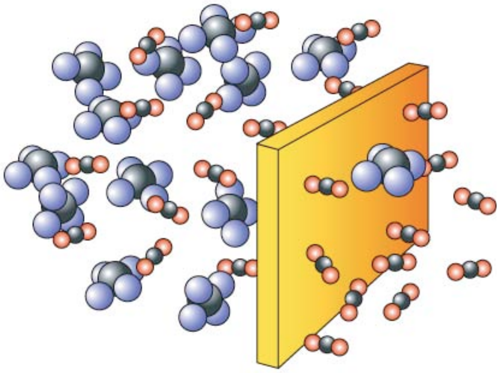


Figure 5. Schematic of a membrane separating a mixture of molecules. Here a mixture of methane (four atoms) and carbon dioxide (three atoms) is depicted. The CO_2 is preferentially passing through the membrane, allowing it to be enriched. Membranes used currently are selective for certain components in a mixture, but most cannot exhibit absolute (or 100%) selectivity for a particular component.

Introduction and Current Status

Highly permeable and exquisitely selective membranes are ubiquitous in nature, where they form the outer walls of cells and govern transport of materials into and out of the cell.[1] Synthetic membranes, made from polymers or inorganic materials, are also widely used in industry as separating devices.[2] A membrane separates species by selectively permeating certain components of a mixture faster than others through a thin barrier in response to an external driving force, such as a concentration, partial pressure or, more generally, a chemical potential gradient (see Figure 5).[3]

Membranes offer a number of inherent advantages over other technologies for separating gases, including

- simple, passive operation with no moving parts
- environmentally benign separation without the use of hazardous chemicals
- small footprint, which is critically important in some applications (e.g., aboard aircraft or spacecraft or on offshore natural gas platforms)
- lower energy use because they can separate species without a phase change

Figure 6 provides some perspective on these attributes with respect to carbon capture. The photograph shows a gas separation membrane unit being used to remove CO_2 from natural gas. The membranes were installed at this facility after an amine absorption system was taken offline because the columns had been corroded by the amine solution previously used to remove CO_2 from the natural gas. The device highlighted in the red box is the membrane system; all other hardware shown in this picture is related to the amine system. The figure provides a compelling example of the reductions in footprint and process complexity that can be achieved by using membranes relative to amine absorption, a current technology for carbon capture. However, the membranes currently used have considerable gaps in capabilities for effective gas separation. To capitalize on the very appealing features of membranes as a transformational means of capturing CO_2, O_2, and other gases important to reducing CO_2 emissions requires development of next-generation membrane materials.

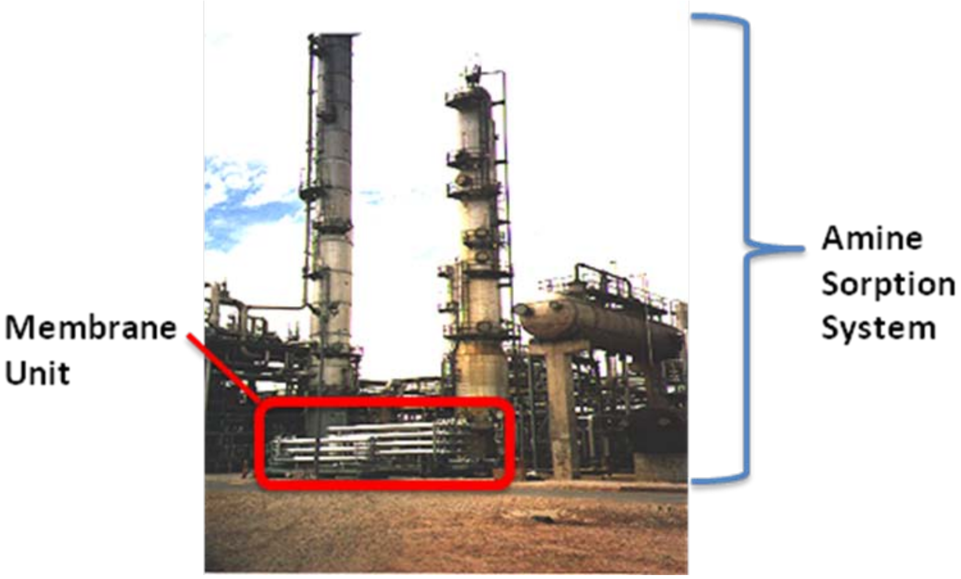


Figure 6. Comparison of a membrane unit with a conventional separation process (i.e., amine absorption system) for removing CO_2 from natural gas. This figure shows the mechanical simplicity of membrane systems as well as their space efficiency relative to other separation processes. Courtesy of Air Liquide.

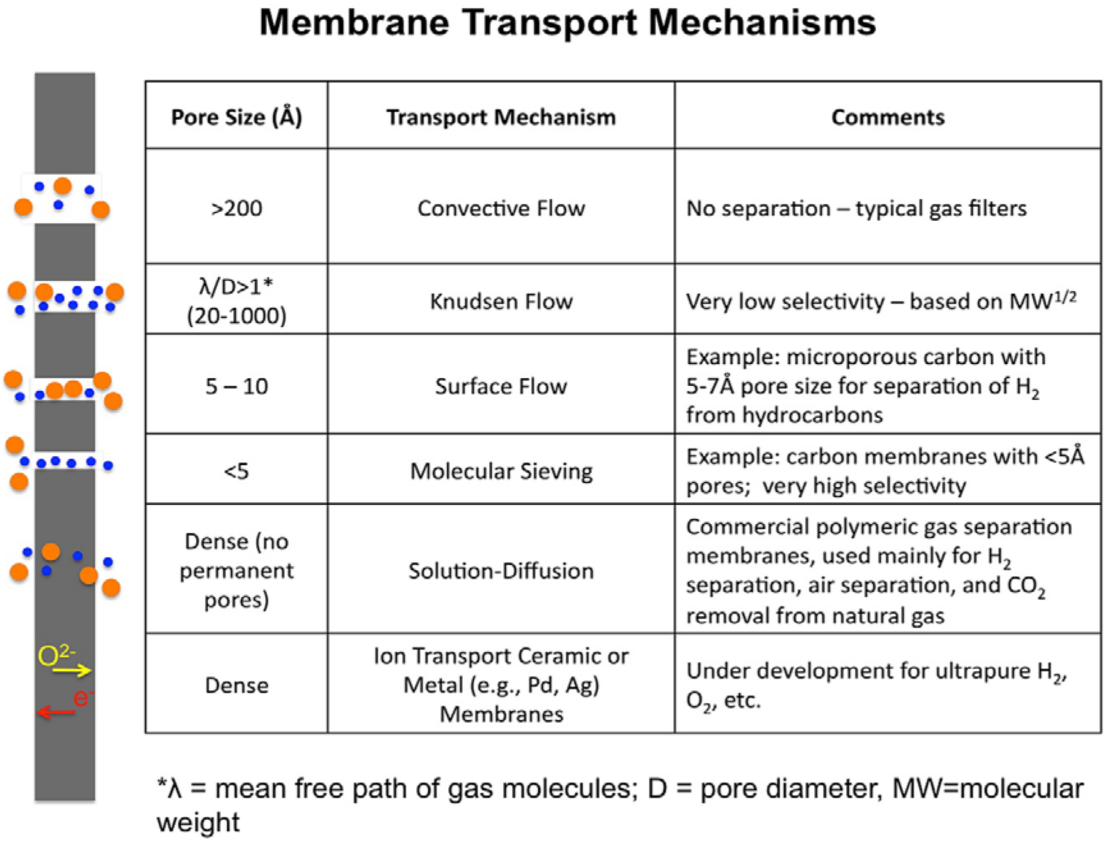
At a molecular level, a variety of mechanisms influence the separation of gases by a membrane (see the sidebar “Membrane Transport Mechanisms”). For example, in polymer membranes, the most widely-used industrial membranes for gas separations, gas molecules are separated according to their relative solubility and diffusivity in the polymer (see the sidebar “Solution-Diffusion Mechanism”). Most polymer membranes currently employed sieve small gas molecules based on size; smaller molecules have higher diffusion coefficients and, in turn, higher permeability coefficients.[4] This size sieving gives the order of gas permeability illustrated in Figure 7, which depicts smaller molecules as being faster (i.e., having higher permeability coefficients) than larger molecules.

Membranes have also been developed that can separate gas molecules based on the relative solubilities of the gases in polymers, with more soluble gases being more permeable than those with lower solubility.[5,6] Gas solubility in a polymer often scales with the critical temperature of the gas.[4] Such polymers are used industrially to remove organic vapors from air or nitrogen streams[7,8] because the membranes are more permeable to the larger, more soluble organic compounds than to the smaller, less soluble air gases. Similarly, polymer membranes that are more permeable to CO_2 than to H_2 are being explored to separate CO_2 from mixtures with H_2.[9]

A gas separation membrane typically consists of multiple layers with different functions. A dense, defect-free ultrathin selective layer, of the order of 100 nm in thickness or less, performs the molecular separation, while a microporous support structure (substructure) provides mechanical strength and minimal transport resistance. A challenge in making membranes is that the selective layer must be very thin to achieve high flux; and as membranes get thinner, it becomes progressively more difficult to prepare them in a defect-free fashion, that is, with no pinholes or other defects that allow convective (i.e.,

Membrane Transport Mechanisms

Molecules can move through (i.e., permeate) membranes by a variety of transport mechanisms. The type of transport that occurs is largely dictated by the sizes of pores or free volume elements in the membrane. The table shows schematically the common types of membrane transport. In membranes with relatively large pore sizes (>200Å), gas molecules permeate by bulk, convective flow. Such membranes have no selectivity for one gas over another. As the membrane pore size decreases, other transport mechanisms, such as Knudsen diffusion and surface flow, can occur. These forms of gas transport, particularly Knudsen diffusion, usually have relatively low selectivity. When the membrane pores shrink further and are only slightly larger than gas molecules (~5 Å), molecular sieving can occur. This type of transport can be very selective; however, with today's technologies, it is difficult to make large-scale ultrathin membranes with this type of pore structure. Alternatively, in the absence of discrete, permanent pores, gas molecules can move through a membrane by solution-diffusion transport. This mechanism involves sorption of the gas into the membrane material, followed by diffusion through tiny, molecule-size free volume spaces in the membrane. Virtually all polymeric membranes currently used commercially for gas separation operate by solution-diffusion. Another mechanism can occur in dense inorganic materials, such as perovskites or metals. It relies on chemical reaction of the gas (e.g., O_2 or H_2) with the membrane material to form ionic species and thus achieve extremely highly selective transport of targeted gases.



Membrane Transport Mechanisms

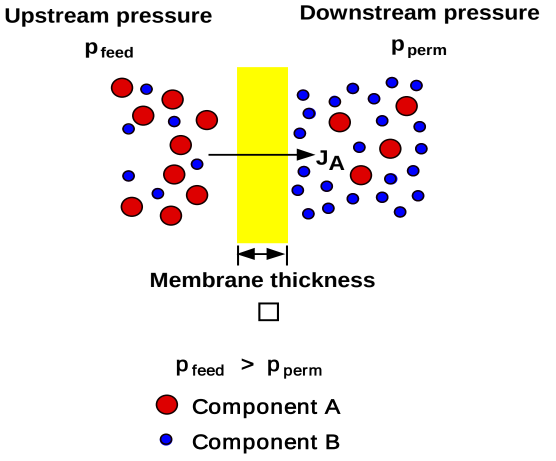
Pore Size (Å)	Transport Mechanism	Comments
>200	Convective Flow	No separation – typical gas filters
λ/D>1* (20-1000)	Knudsen Flow	Very low selectivity – based on $MW^{1/2}$
5 – 10	Surface Flow	Example: microporous carbon with 5-7Å pore size for separation of H_2 from hydrocarbons
<5	Molecular Sieving	Example: carbon membranes with <5Å pores; very high selectivity
Dense (no permanent pores)	Solution-Diffusion	Commercial polymeric gas separation membranes, used mainly for H_2 separation, air separation, and CO_2 removal from natural gas
Dense	Ion Transport Ceramic or Metal (e.g., Pd, Ag) Membranes	Under development for ultrapure H_2, O_2, etc.

*λ = mean free path of gas molecules; D = pore diameter, MW=molecular weight

Solution-Diffusion Mechanism

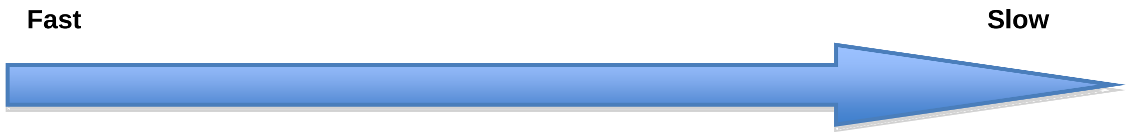
The permeability coefficient of a membrane material for a specific gas is defined as the steady-state flux of the gas through a unit thickness of the membrane under a unit partial pressure driving force. A related parameter used to describe the rate at which gas is transported through a particular membrane is permeance, defined as steady-state gas flux divided by the partial pressure driving force, which is equal to the permeability of a material divided by the membrane thickness. Thus membrane permeance can be increased by either using a higher-permeability material or reducing the membrane thickness.

Permeability is a key factor in the solution-diffusion mechanism that governs the transport of small gas molecules through all polymers currently used as gas separation membranes. In this model, gas molecules first dissolve into the upstream face of a membrane (at high pressure) and then diffuse through the membrane in the direction of decreasing gas partial pressure and desorb from the lower-pressure downstream face of the membrane, as shown in the illustration.[3,4] Within this framework, permeability is a function of the gas solubility (which links the gas concentration in the membrane to the pressure in the adjacent gas phase) and the diffusion coefficient of the gas in the membrane (which is a measure of the gas mobility). The ability of a membrane to separate two gases (e.g., CO_2 and N_2) is often characterized in terms of the ideal selectivity, defined as the ratio of the gas permeabilities. Because permeability is equal to solubility times diffusivity, and selectivity is the ratio of permability coefficients, the membrane selectivity is a function of both solubility selectivity and the diffusion (or mobility) selectivity.



(1) Sorption on upstream side
(2) Diffusion down partial pressure gradient
(3) Desorption on downstream side

- Flux of A $\equiv J_A = \dfrac{P_A\,(p_{feed,A} - p_{perm,A})}{\square}$
- Permeability of A $\equiv P_A = D_A S_A$,
  where $D_A \equiv$ Diffusion coefficient of A
  $S_A \equiv$ Solubility coefficient of A
- Selectivity $\equiv \alpha_{A/B} = \dfrac{P_A}{P_B} = \underbrace{\left(\dfrac{D_A}{D_B}\right)}_{\text{Mobility selectivity}} \underbrace{\left(\dfrac{S_A}{S_B}\right)}_{\text{Solubility selectivity}}$



Gas	H_2O	H_2	H_2S	CO_2	O_2	N_2	CH_4	C_2H_6	C_3H_8	SF_6
D (Å)	2.65	2.875	3.6	3.325	3.347	3.568	3.817	3.8	4.3	5.5
T_c (K)	647.1	33.3	373.4	304.1	154.6	126.2	190.6	305.3	369.8	318.7

Figure 7. Gas sizes (D), critical temperature (T_c), and common order of permeability coefficients of gas molecules in polymers. Gas molecule diameters for H_2, CO_2, O_2, N_2, and CH_4 are from Robeson et al,[10] which provides an analysis of the gas molecule size most relevant for describing permeation properties in polymers. Gas molecule diameters for the other molecules in this table are kinetic diameters from Breck.[11] Critical temperature data are from Reid.[12]

nonselective) flow of gas through the membrane. In this regard, 1 cm^2 of pinholes in 100 m^2 of membrane (i.e., an area fraction of defects of 1 part in 10^6) is sufficient to destroy selectivity in many membranes, so defects or pinholes in the selective layer must be rigorously avoided to achieve high selectivity. The selective layer and substructure can be made from the same or different materials. Typically, the supporting layer has an asymmetric form with a gradient in porosity from a relatively dense portion in contact with the selective layer to a more open section on the opposite side. Figure 8 shows an example of a polymeric hollow fiber membrane used for gas separations.

The thickness of the dense selective layer is very important because it determines the rate at which gases permeate through the membrane, as characterized by membrane permeance. Thinner selective layers translate to higher permeances. High permeance is desirable to reduce the amount of membrane area required to treat a gas stream, and it is particularly important for membrane applications involving large gas streams, such as those considered for CO_2 capture. Today's polymer membranes are all produced by solution casting. The nonporous, dense selective layer, responsible for separating the gases, has a layer thickness of about 100 nm.

Over the past 20 years, interest has increased in inorganic membranes for gas separation, especially for high-temperature gas separations related to synthesis gas production, such as hydrogen recovery and purification and oxygen separation from coal gasification flue gas. Inorganic membranes have also been developed for postcombustion separation of CO_2. While polymer membranes are far more established in this application, the potential for inorganic membranes to operate at high temperatures (>300°C) makes them very appealing for CO_2 separation. Most inorganic membranes have been based on carbon, alumina, zeolites, and silica. Inorganic materials are particularly applicable for the high-temperature oxycombustion process that separates oxygen from air before combustion and produces highly concentrated CO_2 effluents. These materials are based on oxygen-ion-conducting ceramics that separate oxygen with either an ionic conductor or a mixed ion/electronic conductor. To date, dense ceramic membranes have been constructed that exhibit nearly perfect selectivity for oxygen. Purely ionic separation membranes require application of an electrical current across the solid materials to form negatively charged oxygen ions, and the oxygen flux is proportional to the applied current. Thus separations using these materials,

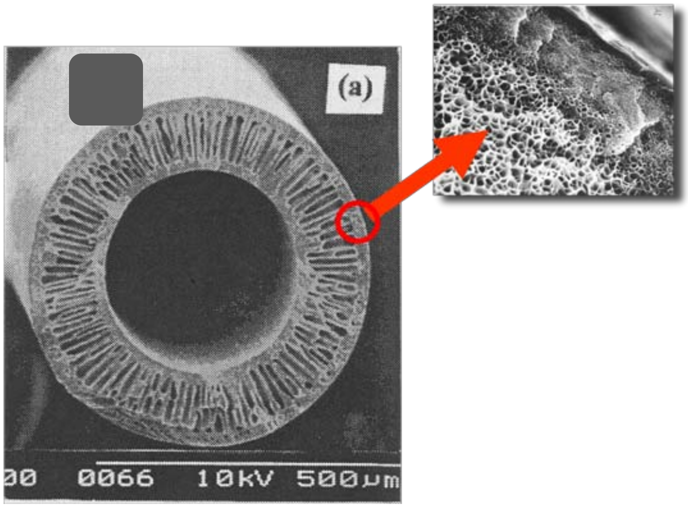


Figure 8. Photomicrograph of a hollow fiber gas separation membrane showing the graded porosity in the wall of the fiber and the ultrathin (~100 nm) separating layer at the outer wall of the fiber. *Source*: D. Wang, K. Li, and W. K. Teo, "Preparation of poly(ether sulfone) and poly(ether imide) hollow fiber membranes for gas separation: Effect of internal coagulant," in *ACS Symposium Series Vol. 744: Membrane Formation and Modification*, eds. I. Pinnau and B. D. Freeman, 96–109 (1999).

which include zirconia doped with materials such as Y_2O_3, Sc_2O_3, and others, may be energy-intensive. Mixed conductors employ electrons in the membrane to combine with O_2 to create negatively charged ions, minimizing or even eliminating the need for current as a driving force for oxygen ion transport. These materials are usually composed of multiple phases that include an oxygen-ion-conducting material, such as doped zirconia, and a conducting material, such as a metal or metal oxide with high electronic conductivity. However, some single-phase materials have been reported that have high oxygen ion conductivity.[13]

Hybrid membranes composed of inorganic materials in a polymer matrix have been reported. These hybrid materials have the potential to bring together the best of both inorganic and polymer materials—offering high-temperature stability, long service life, and enhanced selectivity. Although these materials have high potential, further advances are needed to fully assess their utility in large-scale gas separations.

Existing membranes have limitations that hinder their application in CO_2 capture and other important molecular separations. For example, polymeric membranes are subject to a tradeoff relationship in which materials tend to have high permeability or high selectivity, depending on their chemical structure, but not both.[14,15] This behavior is illustrated in Figure 9, in which H_2/N_2 selectivity, α, is presented as a function of H_2 permeability for many polymers. Each point on this graph represents the H_2 permeability and H_2/N_2 selectivity of a particular polymer. Generally, polymers with high permeability have low selectivity, and vice versa. Materials are more permeable to H_2 than to N_2 because H_2 diffusion is faster than N_2 diffusion in polymer membranes. High selectivity is important to improve the degree of separation possible, and high permeability is needed to reduce the membrane area required to process a given amount of gas. To meet the requirements for efficient, large-scale isolation of CO_2, O_2, or other gases from a complex mixture, it is necessary to develop membranes with *both* high selectivity and high permeability—that is, having properties above the upper bound shown in Figure 9. To achieve such goals will require the development of new classes of membranes, including those made of revolutionary new materials with improved selectivity/permeability characteristics and those incorporating new transport mechanisms.

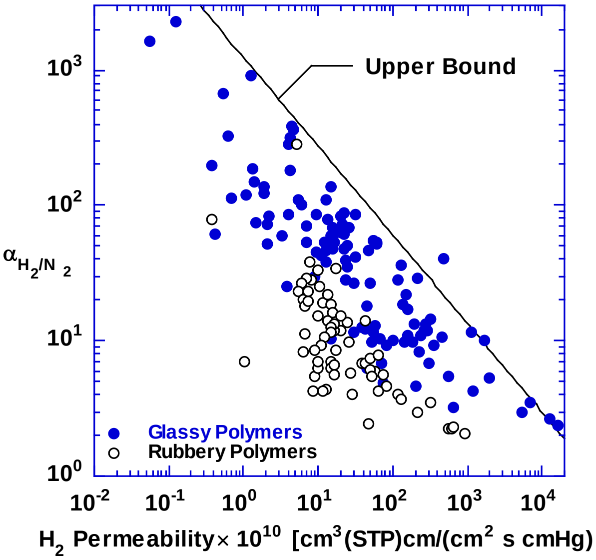


Figure 9. Permeability/selectivity tradeoff as illustrated for the separation of mixtures of hydrogen and nitrogen. Rigid, glassy polymers, which are often more highly size-sieving (i.e., have higher diffusivity selectivity) than flexible, rubbery polymers, populate the frontier of this cloud of data points; the line, called the upper bound, provides a measure of the best known combinations of permeability and selectivity.[14,15] Revolutionary new membranes are needed to achieve permeability/selectivity characteristics beyond the upper bound limitations.

Currently available membranes have other issues that limit their practical applications for gas separations. In challenging operating environments, such as those expected for CO_2 capture, the performance and mechanical stability of membranes can be compromised. Harmful contaminants in the gas streams, as well as high temperatures and/or pressures, can adversely impact membrane performance and long-term productivity. For example, in polymer membranes, phenomena such as plasticization induced by highly sorbing species reduce the size-sieving ability. Consequently, the gas permeability observed in single-gas experiments often appears much more promising than results from real systems that contain mixtures of CO_2 and other components, such as methane, nitrogen, and hydrogen. In metal membranes, trace components, such as sulfur compounds, poison the membrane surface and ultimately limit transport of the desired molecules. There is a clear need for robust materials that can be fabricated into complex membrane structures while maintaining good transport properties. However, development of these next-generation materials will require new understanding of the separation mechanisms in these material, as well as new strategies for materials synthesis and new capabilities in computational tools to guide the design of robust materials and model their performance.

Most of today's best-performing polymer membranes are highly amorphous, nonequilibrium glassy polymers. Consequently, another challenge for current membranes is time-dependent behavior caused by physical aging. Figure 10 shows an example of this effect for a polyimide used for nitrogen production from air.

The main limitation of oxygen separation via inorganic membranes is that a thinner membrane is needed for higher conductance, and as membrane thickness decreases, so does stability. In addition, in mixed-ion electronic conductor membranes used for O_2 separation (which are based on converting the gas to oxygen anions), as the membrane becomes thinner to achieve high conductance, the separation efficiency drops as the reaction between the membrane material and the gas becomes limiting.

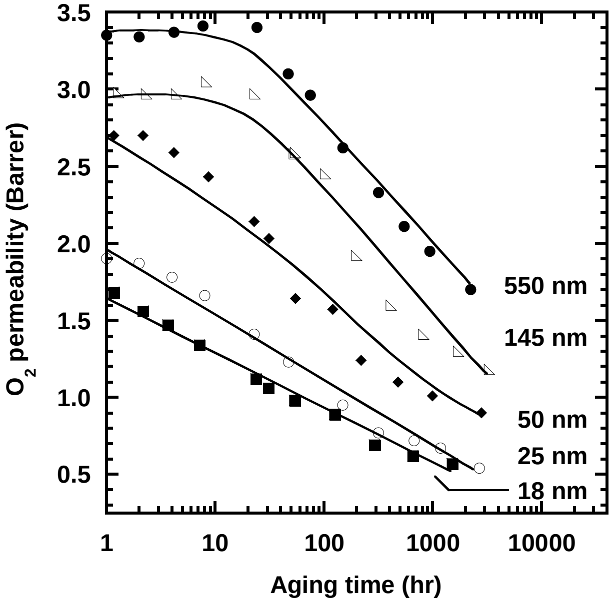


Figure 10. Effect of membrane thickness and time on gas permeability properties of Matrimid®, a glassy polymer. For reasons that are not well understood, the physical aging process, and therefore the permeability, becomes dependent on membrane thickness once the thickness is less than about 1 micrometer. As the figure indicates, permeability differs by more than a factor of 6 when a relatively thick (550 nm) membrane at just a few hours past the start of the aging experiment is compared with an ultrathin (18 nm) membrane aged for about 1000 hours. These measurements were conducted at 35°C and at an oxygen pressure difference of 2 atm across the membrane.[16]

Current membranes are typically gradient structures, comprising either multiple layers of different materials (e.g., multilayer composite membranes), variations in membrane material density through the structure of the membrane (e.g., asymmetric membranes), or both. The development of these structures has evolved in a largely Edisonian fashion. To achieve high performance and maintain integrity in operation—where membranes may be exposed (and respond) to gradients in pressure, temperature, and other parameters—the interfaces between different materials in a membrane or between regions of different density are critically important. As new membranes are developed, with ever thinner selective layers, the effect of the interface on the transport properties and robustness will become even more important. However, there is a large gap in the fundamental understanding of rational manipulation of interface properties to achieve desired structures (e.g., tailored 3D architectures) while maintaining the required robustness and outstanding transport properties.

Currently, all synthetic polymer membranes are processed from solution in organic solvents, using processes such as those presented in Figure 11. This is the only known commercially feasible, large-scale method of making ultrathin gas separation membranes. However, because the membranes are soluble in organic solvents, the membranes are inherently sensitive to chemical attack by organic contaminants that are present in many emission streams. One potential route to resolving this conundrum involves solution processing of the materials as soluble precursors, followed by conversion into highly stable, robust, high-performance membranes using chemical processes initiated by heat, light, or microwave radiation, for example.[17] The use of organic solvents in membrane processing has deleterious effects, however, because it contributes significantly to the cost of membrane manufacture and ultimately requires disposal of the solvents. The development of solventless strategies to prepare the multilayer structures required for high-performance gas separation membranes

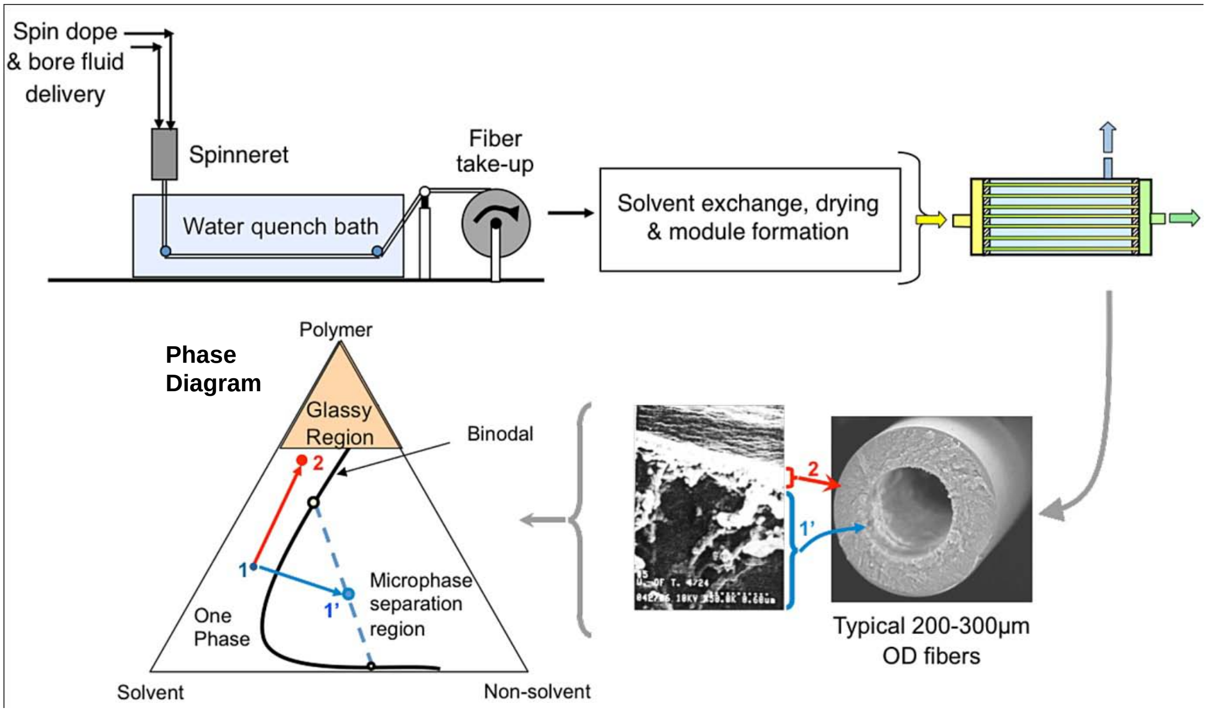


Figure 11. Forming asymmetric hollow fiber membranes involves solution processing of polymers to a highly nonequilibrium state. The spin dope (labeled 1 on the phase diagram) contains polymer dissolved in solvent and potentially other additives. This dope is fed to a spinneret and the nascent fiber is extruded into a nonsolvent quench bath (typically water), which precipitates a rapid phase separation process (1 → 1') to form the porous support structure. After leaving the spinneret and before entering the quench bath, solvent evaporates from the outer surface of the fiber (1 → 2 on the phase diagram), forming the dense skin, which is the selective membrane. When this skin is quenched in the bath, the polymer in the separating layer is kinetically trapped in a nonequilibrium state. Courtesy of Professor W. J. Koros, Georgia Tech.

would mean revolutionary improvements in the efficiency of membrane preparation and provide access to new families of materials that could be used. Such processes could employ self-assembly of polymeric materials into hierarchical structures, taking a cue from processes found in nature.

To achieve a 90% reduction in CO_2 emissions from existing coal-fired power plants, current membrane processes will use about 20% of the electricity generated.[18] Therefore, there is a need to dramatically reduce the amount of energy required for separation to minimize the impact on process requirements. Energy requirements could be reduced by breakthroughs in membrane materials with unprecedented transport properties and by harnessing alternative driving forces for separation. The major bottlenecks to reducing the energy required by membranes to efficiently capture carbon are

- enhancing membrane selectivity while reducing requirements for energy-intensive temperature and pressure swings
- overcoming the tradeoff between membrane permeability and selectivity
- addressing the limited chemical and thermal stability of membranes
- enabling the design and fabrication of controlled membrane architectures

Basic Science Challenges

Much of the progress in membrane-based separations has been obtained by optimizing existing technologies. Such incremental advances will not meet the daunting challenges that carbon capture entails. Fundamental research is needed to enable the revolutionary breakthroughs required to produce effective membrane separation systems in the future. It is clear that there are a multitude of physical and chemical processes involved in the separation of multicomponent gas mixtures using membranes—all of which occur at the atomic and molecular level—and huge gaps in the knowledge of these processes. A further requirement of membrane materials is that they be designed to operate in extreme conditions (e.g., temperature, reactive chemicals); thus the stability and lifetimes of the materials must be carefully considered. Finally, separation processes are often driven by energy-intensive methods requiring changes in temperature and/or pressure to effect separations. Developing new membranes that meet the requirements for future carbon capture technologies is a challenge that requires breakthroughs in materials and chemical processes. The following research areas were defined.

- Elucidate the atomic- and molecular-level processes that affect separation performance in membranes, including mechanisms of neutral, ion, and electron transport through a membrane. For example, in the case of mixed ion-electronic membranes used for O_2 separation, understanding interfacial reactions could make it possible to optimize conversion and transport of ionic species. Once these myriad processes are understood, materials architectures could be designed to optimize separation, perhaps taking advantage of hierarchical structures, hybrid organic/inorganic structures, tailored functionalities (including catalytic sites), and other features to enhance transport and selectivity and improved stability (i.e., chemical, thermal, and mechanical stability).
- Discover new approaches for driving membrane separations, including harnessing alternative driving forces or specific membrane-permeate interactions that can enable membrane-based separations that are less energy-intensive than conventional temperature and pressure swings. For example, an applied magnetic field might be used to alter the transport of a gas through a membrane channel.
- Realize revolutionary concepts for the design of membrane separation systems that are inspired by nature, incorporating self-assembly and even self-repairing strategies, multifunctional structures, and wholly new approaches to achieve highly selective separations. Such processes could incorporate hybrid materials and even "smart" materials that would alter the transport of a targeted gas or ion upon application of a specific external trigger.

All of these scientific challenges will require significant advances in characterization tools that can monitor multiple physical and chemical processes simultaneously under realistic conditions. Results from characterization studies will require advanced computational tools for modeling complex systems, which can, in turn, be used for designing materials, structures, and driving forces that will be incorporated in a new generation of membrane separation processes for reducing CO_2 emissions.

Conclusions

Separation based on membranes offers extraordinary promise for low-energy, efficient, reliable and environmentally benign gas separation for carbon capture applications. However, to realize the full potential of this technology, basic research is urgently required to provide revolutionary new membrane materials with controlled architectures that can respond efficiently to alternative driving forces. Recent advances in the synthesis of tailored materials, especially those with nanoscale architectures and functionalities; characterization tools; and molecular simulation and modeling techniques provide unprecedented new opportunities to develop the next generation of high-performance, robust, scalable membranes for carbon capture processes.

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PRIORITY RESEARCH DIRECTIONS

INTERFACIAL PROCESSES AND KINETICS

Abstract

Mass transfer across the gas-liquid interface can be the rate-limiting step controlling the uptake and release of carbon dioxide. A key barrier to the development of greatly improved liquid absorption separation processes is the lack of understanding of the nature of gas-liquid interfaces. Once understood, this information could be used to design specific modifications to those interfaces to enhance gas separation systems. Advancing knowledge in this area will require the strong coupling of theory and experiment with the assembly of interdisciplinary expertise in the structures of liquid, physics of interfaces, molecular spectroscopy, and chemical kinetics. In addition, new approaches are needed to characterize dynamic and chemically complex interfaces—examining both the spatial and temporal distribution of solution components and reactants in the interface.

Background and Motivation

The gas–liquid interface is the gateway to bulk absorption. Transfer across this boundary is well known to limit many CO_2 process rates. Therefore, it plays a critical role in any carbon capture process using a liquid. Liquids are intrinsically difficult to study since they are disordered and have a time-varying, dynamic structure. Even less is known about the chemical structure of liquid–gas interfaces. Surface composition is not a simple termination of the bulk structure but rather is dictated by minimization of surface free energy.

Mass transfer considerations suggest that kinetic modifications of CO_2 absorption processes are best targeted very near the surface to maximize flux into the bulk. Understanding the structure and dynamics of this interface is key to tailoring uptake and release kinetics and will allow controlled design of future sorption materials.

Interfaces warrant study to avoid potential kinetic bottlenecks; understand the structure and dynamics of complex liquid–gas interfaces; and understand the linkage among the composition, structure, and chemistry of the interface. Liquids potentially useful for carbon capture, oxygen purification, or other gas separation approaches are likely to be complex systems such as highly concentrated basic solutions, ionic liquids, or exotic multiphase fluids—but we don't really understand even simple fluids yet. For example, even relatively low-concentration aqueous salt solutions have been predicted to have an asymmetric distribution of anions and cations at the vapor–liquid interface (Figure 12), a result confirmed by recent experiments.[1]

Research Directions

A key barrier to the development of greatly improved liquid absorption separation processes is the lack of understanding of the nature of gas–liquid interfaces. That understanding, once obtained, could be used to design specific modifications to those interfaces to enhance gas separation systems. Advancing knowledge in this area will require the assembly of interdisciplinary expertise in the structures of liquids, the physics of interfaces, molecular spectroscopy, and chemical kinetics. In addition, new approaches are needed to characterize dynamic and chemically complex interfaces—examining both the spatial and temporal distribution of solution components and reactants in the interface. Current experimental tools have shown that the surface composition can be strongly segregated, and additional knowledge needed to understand dynamic separation processes will also require temporal resolution. Experimental approaches are needed to enable in situ probing of liquid interfaces, capturing the molecular processes that occur during active transfer of gas across the interface. Understanding of the distribution of absorption phenomena that are primarily molecular versus those that are reactive, and the interplay between the two, will be required to both predict and design better interfacial properties for enhanced gas separation systems. By varying the chemical nature and composition of the liquid, it may be possible to tailor and control the gas–liquid interface so as to improve the overall reversibility and switchability of the sorption reactions. These goals will require strong coupling of experiment and theory, including experimental probing and computer simulation of liquids with greatly improved spatio-temporal resolution. Ideally, these dynamic interfaces could be chemically imaged with atomic-scale spatial resolution on time scales ranging from femtoseconds to minutes.

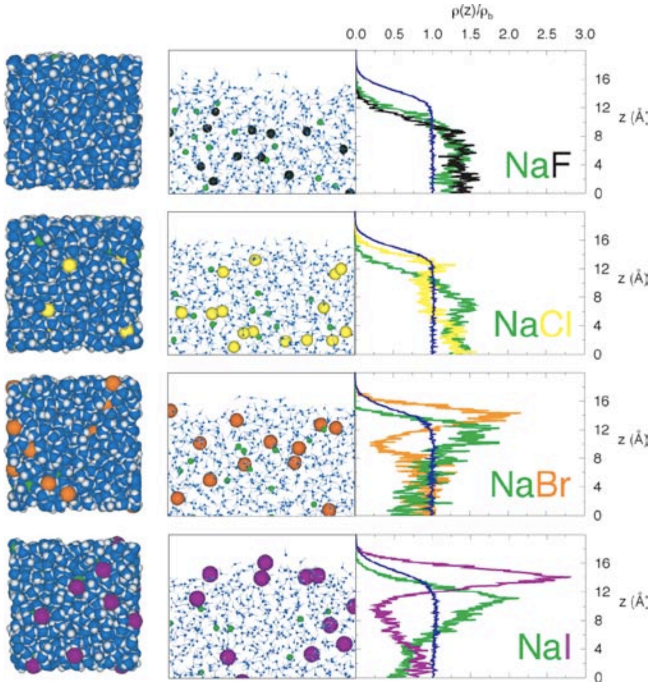

Figure 12. Snapshots (top and side views) of the solution–air interface of 1.2 M aqueous sodium halides from molecular dynamics simulations and number density profiles of water oxygen atoms and ions plotted vs distance from the center of the slabs in the direction normal to the interface, normalized by the bulk water density. Notice the preferential segregation of the more polarizable anions Br and I to the interface.[2]

Reactions at solid surfaces are routinely studied today—for example, catalysis on solids is a mainstay of surface science. That level of understanding is not available for liquid–gas interfaces, and reactive processes in these gas capture systems are also critical phenomena. For most CO_2 capture processes, the rate of chemical reaction can be the most important determinant of the transfer rate across the interface. Rational design of improved processes can be expected to locate catalytic functions in the interface, both to improve chemical reaction rates and to improve the physical characteristics of the surface through functions like surfactants. Chemically tailored structures that self-organize these functions at the correct interface locations will be required to optimize interface function in capture systems. These tailored systems can become the foundations of facilitated transport mechanisms similar to those prevalent in biological systems.

Scientific Questions and Opportunities

A key scientific question is to understand the concentration and chemical state of targeted gases and associated materials at liquid interfaces. For CO_2, such materials at the interface may include molecular CO_2, carbonate/bicarbonate, and stronger complexes such as the carbamates that occur in amine solutions. Further, it is important to understand how this chemistry changes as materials transfer from the surface into the bulk. Such distance-dependent composition changes also exist in static systems, but they are even more crucial to understanding and predicting mass flux across the interface of an active gas capture system. Addressing these issues will require surface-specific spectroscopies to avoid interference from the bulk. Depth profiling at the very small scale—perhaps as small as a few molecular diameters—is required. Tools are becoming available to probe time-averaged structure and composition (e.g., vibrational sum frequency generation, photoemission from liquids, x-ray and neutron scattering). Ideally, spectroscopic tools and techniques with sufficient temporal resolution would be available to study the kinetics and dynamics of absorption/desorption phenomena. Tools of this quality will require the development of new experimental methods and instrumentation that are capable of working in coexisting gas–liquid environments (moving from high vacuum to high pressure). At the solid–liquid and solid–vapor interfaces, probe microscopies like scanning tunneling microscopy and atomic force microscopy have provided a wealth of information about dynamics and reactivity. The liquid–vapor interface is far more dynamic, so extracting this type of information is presently unfeasible. New approaches are needed to extract comparable information.

The combination of theory and experiment has led to an unprecedented level of understanding of how ions are distributed at the aqueous–air interface of salt solutions. Owing to the more complex nature of the liquids envisioned for capture processes, the combination of theory and experiment that will be available with exascale computing suggests that major improvement in theory will be possible within the next decade. The challenge is to describe liquid–vapor interfaces of more complex fluids, incorporating explicit interactions with the vapor phase, capturing static and dynamic features, and especially capturing reactions at the interface. First-principles simulation based on density functional theory has proved invaluable for studying reactions at the solid–gas interface, and only today are methods becoming available for the solid–gas. The liquid–gas interface, because it is disordered on both sides, becomes much more difficult.

Exascale computing and new experimental methods will permit the development of the fundamental understanding necessary to allow rational design of novel liquid interfaces for CO_2 capture and other separation processes (e.g., O_2). With enhanced understanding of the details of interface structure and chemistry, it will be possible to design interface properties that enhance capture rates and eliminate transfer resistances that currently constrain large-scale capture systems. This rational design of interfaces will incorporate the modification of surface physical properties and the catalysis of key chemical reactions responsible for enhancing transport across the interface. It will also improve the handling and environmental characteristics of industrial fluids for which a very large surface area is both an operational requirement and a major limitation because of evaporation, oxidation, and other deleterious side reactions.

Potential Impact

Advances in this area can be expected to increase the understanding of liquid–gas interfaces and complex solutions. This will be the foundational underpinning of rational design of new materials and processes with enhanced capture capacity and reduced energy demand for regeneration of CO_2 and other purified gases. These advances could allow capture device performance near the thermodynamic limit. Understanding gained in these studies could also find practical application in such diverse areas as catalysis, atmospheric science, and ocean–atmosphere interface questions.

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NOVEL SOLVENTS AND CHEMISTRIES

Abstract

Gas separation via absorption is intimately connected with the physical and chemical properties of the gas–liquid system. The goal of this PRD is to develop the fundamental insights necessary to exercise exquisite control over this combination. Achieving this goal will require deep understanding of complex gas–liquid systems, especially the factors that govern selectivity and solubility, determine non-ideal behavior, and determine other important physical properties. It will require the ability to model, simulate, and predict these properties. It will require us to be able to discover liquid systems with chemistries carefully optimized to particular separations. And most important, it will require that we be able to close the loop, to combine experimental and theoretical insights to design and synthesize highly efficient and robust liquid separation systems.

Background and Motivation

The physical and chemical properties of a liquid absorbent are key to its performance in a gas separation. As shown in Figure 13, the absorbent, A, must be able to accommodate the targeted gases, in this case, CO_2, to the exclusion of others, typically as a result of differences in physical solubility. This physical solubility is controlled by the intermolecular interactions among absorbent molecules themselves and between absorbents and gases. These interactions are generally understood for simple fluids but not nearly as well for fluids as structurally and compositionally complex as those of interest for gas separations. It is further advantageous to have the absorbent chemically react with a target gas, such as CO_2, to increase solubility. The isotherms that describe the absorption and desorption of gases, and the rates of transfer to and from the liquid phase, are ultimately controlled by these interactions and mechanisms.

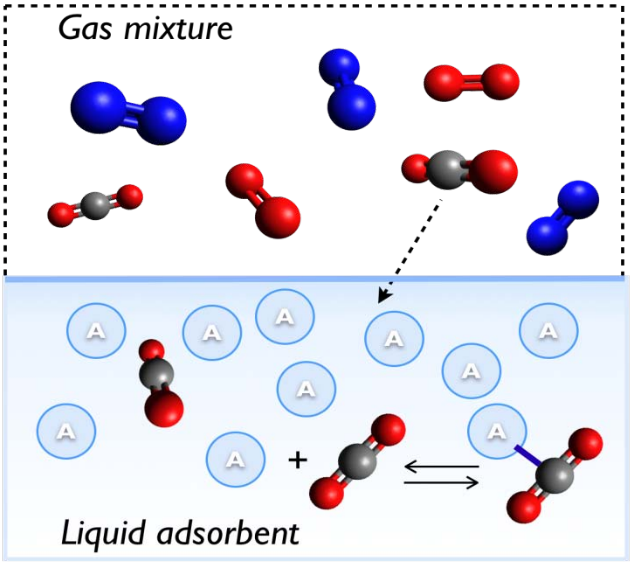


Figure 13. Schematic of CO_2 selectively isolated by dissolving in a liquid and its subsequent chemical reaction with absorbent, A. CO_2, represented by the one atom of carbon (gray) and two atoms of oxygen (red), is initially in a mixture of O_2, two red atoms, and N_2, two blue atoms.

Liquid absorbents for CO_2 separations can be categorized into several classes, including water itself, chemically modified aqueous systems (including amines and nonaqueous organic solvents), and nonaqueous hybrids, like ionic liquids (see the sidebar "Ionic Liquids: Nonvolatile Solvents for CO_2 Capture"). Each class of absorbent presents its own challenges to understanding the thermodynamics and kinetics of gas separation. The current level of this understanding is far from what is needed to exploit known absorbents; further, other classes of absorbents remain to be discovered.

The overarching challenge and opportunity is to use understanding to drive discovery of radically new, more efficient adsorbents that enable energy-efficient gas separations.

Ionic Liquids: Nonvolatile Solvents for CO_2 Capture

Ionic liquids are a new class of salts that are liquid in their pure state near or below ambient temperatures. This sets them apart from common salts such as their familiar cousin sodium chloride (table salt), which melts at around 800°C. The oppositely charged ions in table salt are small (Na^+ and Cl^-) and pack neatly into an ordered, stable crystal. In contrast, large inorganic or organic ions are found to pack more loosely and thus to form low-melting ionic liquids.

Ionic liquids are being investigated for CO_2 capture because they have many unique and highly desirable properties. They have a high intrinsic physical solubility for CO_2, and even higher CO_2 capacities can be achieved by adding functional groups that chemically react with CO_2. They have high thermal stabilities, making them attractive for use in precombustion and postcombustion CO_2 capture. They have essentially no vapor pressure, meaning they will not evaporate during use, and novel regeneration strategies may be possible. Most important, by altering the cation, anion, and functional groups, an almost limitless number of ionic liquids can be prepared, suggesting a rich area for future research.

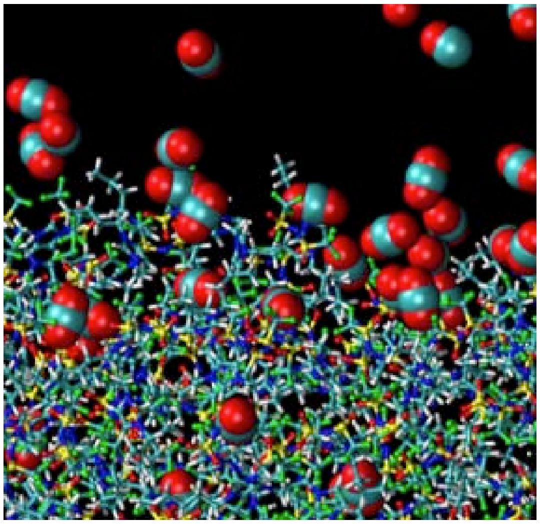


Image from a molecular simulation showing CO_2 (two red oxygen atoms and a gray carbon atom) absorbing into the ionic liquid 1-ethyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide. Courtesy of E. Maginn, University of Notre Dame.

Research Directions

Fundamental understanding of intermolecular interactions of gases dissolved in liquids

The liquid state exists because of the intrinsic intermolecular interactions among the molecules. These interactions can be of many types and ultimately control the physical characteristics of the liquid, such as its density, viscosity (or resistance to flow), and boiling point. For single-component, simple liquids characteristic of physical solvents, these intermolecular interactions and their consequences are fairly well understood from both extensive experimentation and classical molecular simulation. However, for liquids that have additional types of interactions, such as electrolytic liquids (e.g., aqueous, ionic liquids) or structured liquids (e.g., microemulsions) the connections among structure, composition, temperature, pressure, and physical properties are only now becoming understood.

Separation of gases via absorption introduces additional layers of complexity to understanding intermolecular interactions in liquids because of the myriad physical and chemical phenomena that occur in these complex mixtures. Simple physical dissolution of a gas into a liquid can dramatically alter important physical properties of the liquid. Models exist for describing how the properties of gas-liquid mixtures depend on the proportion of the two components in relatively simple liquids. For example, when the amount of gas in the liquid is small, the proportions can be described using Henry's Law, which states that the amount of dissolved gas is simply proportional to pressure. However, Henry's Law breaks down as the amount of dissolved gas gets large, and it may have limited applicability in more complex liquids.

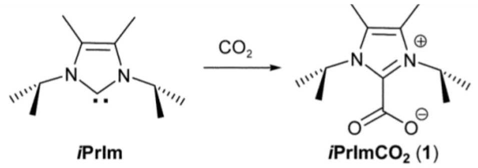
Because the key to separation by liquid absorbents is the *selective* incorporation of one gas over many others, it is important to understand and control the intermolecular interactions that govern this physical selectivity. These interactions get even more complex when one considers absorbents that undergo chemical reactions with a target gas molecule (e.g., CO_2) because both physically and chemically bound molecules are present in different proportions, which change depending upon solution conditions.

Understanding these many aspects of intermolecular interactions that contribute to gas separations in liquids requires characterization methods to elucidate key physical and chemical properties of these interactions, especially in complex mixtures and under reactive conditions. The insights gained by these measurements will serve as a foundation for developing new computational models to predict these interactions. Together, this understanding will catalyze the development of new absorbent systems with precisely tailored properties to yield vastly improved separation selectivity and efficiency.

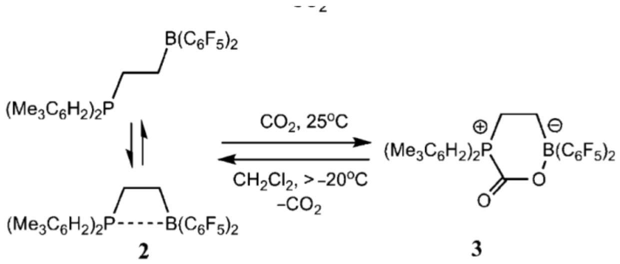
New chemistries, new absorbent systems

A major challenge in large-scale absorbent systems is to devise a means of reducing the energy required for separations, whether it be a change in temperature or in pressure. As stated in the Liquid Absorbents panel report, oxygen is selectively isolated from air in blood with highly selective, cooperative, and reversible binding of O_2 to hemoglobin. Nature has an analogous system for isolating and transporting CO_2 in plants and animals using carbonic anhydrase. Using nature as inspiration, can new chemistries be devised to isolate targeted gases from a complex mixture selectively and efficiently? A potential advantage of such an approach is that the driving force of such reactions could lower the energy required for the separations. However, for applications in large-scale separation schemes, the molecules developed for nature-inspired separations will need to be stable over many cycles of reuse. Thus the scientific challenge is to design highly specific and robust chemical systems with tailored physical and chemical properties for optimized separations.

Is this vision possible—can molecules be designed to react stoichiometrically, reversibly, and in a controlled fashion with CO_2? Evidence suggests the answer is yes. Imidazolium carbenes were noted to have this ability in work reported first in 2004:[1]



Here the Lewis acidic CO_2 molecule binds to the Lewis basic carbene center to form the product carboxylate on the right. This reaction can be reversed by heating or by reducing the CO_2 pressure, or the carboxylate intermediate can be further reduced to methanol.[2] More recently, bifunctional “frustrated” Lewis acid–base pairs (see “Getting a Grip on CO_2”) have been exploited to the same end:[3]

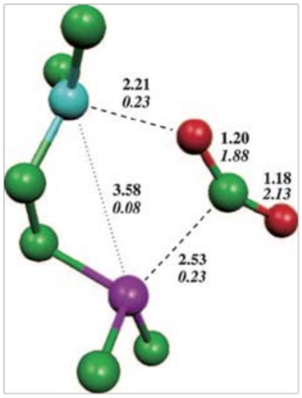


Getting A Grip on CO_2

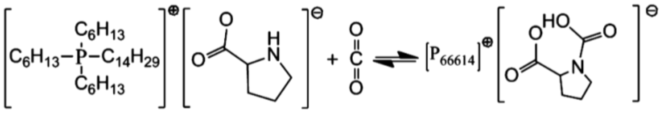
Acids and bases are the *yin yang* of chemistry—opposite yet interconnected forces behind chemical bonding and reactions. In the Lewis definition, an *acid* is an electron pair acceptor and a *base* an electron pair donor. When brought together, the female acid and male base tend to combine to form an acid-base bair, neutralizing each other. Most common molecules are thus either Lewis acidic or basic, but not both.

Frustrated Lewis pairs are cleverly designed molecules that break this rule.[4] These molecules contain acidic and basic elements linked together in a way that prevents the two from internally neutralizing one another. These frustrated systems can promote normally difficult reactions, such as the heterolytic splitting of H_2. CO_2 as a molecule is Lewis acidic—the C center is electron-deficient and likes to behave as an electron pair donor, as in its reactions with amines described in the sidebar “Aqueous Amines for CO_2 Separation” in the liquids panel report.

The O centers are weakly Lewis basic, becoming more so when CO_2 combines with a base. This internal *yin yang* can be exploited in reactions with frustrated Lewis pairs. As shown in the image, a properly designed frustrated pair (purple, basic phosphorus, and light blue, acidic boron) can put a pincer grip on CO_2, grabbing both the more acidic carbon (green) and somewhat basic oxygen (red).[3] Because both the shape of the pincer and the strengths of the acidic and basic ends can be tuned, frustrated pairs hold promise for reversible CO_2 capture.



Ionic liquids have been functionalized to have similarly selective reactions with CO_2, and the locations of the tethered groups on either the cation or anion have been shown to provide an additional level of control over the reaction equilibria:[5,6]



Here, the prolinate anion combines with CO_2 to form the carbamate anion on the right, leaving the spectator $[P_{66614}]^+$ phosphonium cation unchanged. And finally, as described further below, solvents that reversibly form ionic liquids in the presence of CO_2 have been developed.[7] While challenges remain in translating any of these chemistries into a practical separation system, they give a good hint of the potential for designing new approaches to driving gas separations using chemical reactions.

Even within a given chemistry, the number of possible chemical permutations is enormous. Combinatorial synthetic methods could provide one way of developing chemical libraries and can be combined with rapid screening to identify candidates. We need similarly efficient approaches to characterize the new absorbents for all the important properties (e.g., isotherms, viscosity, thermal stability, chemical stability) and how these properties change in response to external stimuli, down to the molecular scale, simultaneously, and in situ. Coupling to fully predictive computational models would revolutionize the ability to design candidates with optimized selectivity and efficiency. New computational tools would allow the same range of key properties to be predicted and enable insightful computational "experiments" that would be difficult or even impossible to perform in the laboratory. Coupling computational simulation and experiment is obviously essential to validating models and to developing the physical and chemical insights that would form the basis for the development of new absorbents.

A further critical issue is the *rate of reaction* between absorbent and gas. Water itself can be used to separate CO_2 from flue gas through the formation of bicarbonate:

$$CO_2 + H_2O \rightleftarrows HCO_3^- + H^+ \ ,$$

but the reaction rate is too low for practical use. Catalysts can be used to speed up this process, as happens in the body (see the sidebar "Carbonic Anhydrase"). Translating this or other catalytic approaches to the challenging environment of a real gas separation will require major advances in chemistry.

The large scale of CO_2 separations implies the use of large quantities of absorbent, even for the best materials that can be identified. A modest-sized 500 MW power plant produces on the order of 22 kmol CO_2/s and would require on the order of 1000 metric tons of absorbent, based on simple order of magnitude estimates. For absorption to be practically useful, then, we need not only to discover new CO_2 chemistries but also to discover synthetic strategies for absorbents that have very high atom and energy efficiency from low-cost feedstocks. Can absorbents be prepared from CO_2 itself, for instance, or coupled somehow to the CO_2 separations? What inexpensive feedstocks can be used to make nontraditional absorbents?

Predict and exploit nonideal absorption

For thermodynamically driven separations, the equilibrium between gas and liquid phases, as embodied in absorption isotherms, ultimately determines the effectiveness of a material for a separation. To achieve energy-efficient separations, control over chemistry must be accompanied by control over isotherms. These isotherms are determined both by the enthalpy and the entropy ΔS° of absorption, through $\Delta G^\circ(T) = \Delta H^\circ(T) - T\Delta S^\circ(T)$ (e.g., if the absorbent reacts with the gas $\ln K_{eq} = -\Delta G^\circ/RT$, where K_{eq} is the equilibrium constant).

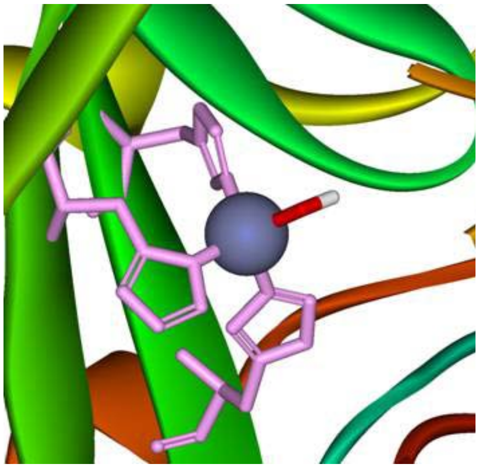
Carbonic Anhydrase: Biomolecules that Reversibly Catalyze CO_2 Hydration

Carbonic anhydrases are enzymes that catalyze the hydration of carbon dioxide and the dehydration of bicarbonate:

$$CO_2 + H_2O \rightleftarrows HCO_3^- + H^+$$

This reversible reaction can be exploited to separate CO_2 from other gases. These carbonic anhydrase-driven reactions are of great importance in a number of human tissues, where they are important in facilitating diffusion and transport of CO_2, secretion of bicarbonate and protons, and maintaining acid–base and fluid balance. In particular, carbon dioxide generated by metabolism in all cells diffuses to red cells in the blood, where carbonic anhydrase catalyzes the formation of bicarbonate for transport to the lungs. In the lungs, carbonic anhydrase catalyzes the formation of carbon dioxide for exhalation.

Carbonic anhydrases in humans consist of a single polypeptide chain with a zinc atom complexed by three histine ligands. These enzymes are among the fastest catalysts known; at low concentrations of CO_2 and HCO_3^-, the reaction is limited by diffusion; and at high concentrations, the turnover rate is 10^6 reactions per second per mole enzyme. Catalysis of this reaction is reversible. CO_2 hydration is catalyzed by the enzyme-bound zinc-hydroxide, whereas bicarbonate reacts with the zinc-water form of the enzyme ($pK_a \sim 7$).



Closeup of active site of carbonic anhydrase isozyme IIshowing three histidine residues and hydroxide coordinating zinc. Image courtesy of Wikimedia Commons.

In an ideal absorption system, the enthalpy of absorption is independent of the amount of absorbed material. Ideality gives the familiar Henry’s Law behavior for physical absorption and Langmuir behavior for chemically reacting absorbents. Real absorbents always deviate to some extent from ideality: the absorption of one molecule of gas has some influence on the absorption of the next. The opportunity is to control these interactions. For instance, can we design absorbents that exhibit *cooperativity,* in which the absorption of one gas molecule *promotes* the absorption of the next? Cooperativity is accomplished in hemoglobin through the chemical linking of four porphyrin rings; can similar effects be achieved in molecules suitable for industrial gas separations?

For an efficient separation system, the adsorbent should have a high *capacity* and *selectivity* for the species being separated, which generally translates into a large exothermic heat of absorption, ΔH°. However, this enthalpy must be paid back during the regeneration step, when the absorbate is separated from the absorbent, and thus easy regeneration demands low ΔH°. For thermodynamically based separations, then, these two objectives would appear to be at odds with each other. However, the absorption entropy provides a separate thermodynamic handle on separations. Can differences in sizes and shapes (entropy) of components to be separated be exploited as an alternative strategy to using differences in interaction energy (enthalpy)? Can strategies be developed to control absorption enthalpy and entropy in as independent a manner as possible? What are the limits on this independent control? These challenges would provide immense improvements in the cost and practicality of large-scale use of liquid absorbents for separation of CO_2 and O_2 from complex mixtures and would have broad impact on other applications of gas separation.

Scientific Questions

Absorbent-based gas separations essentially exploit the physical chemistry of gas–liquid equilibrium and reactions. The understanding of these interactions has advanced enormously over the years. CO_2 capture (and O_2 concentration) elevates these questions to a new level, however: Can they be described, understood, and modeled in the context of a gas mixture as complex as a flue gas, over the wide range of conditions that an absorbent will experience? Even more fundamentally, can they be controlled so as to minimize the energy cost of separations? And finally, can this control be realized in systems that meet all the other practical constraints of a real-world separation?

Potential Impact

This PRD touches on some of the most fundamental questions of intermolecular interactions and reactivity. This scientific knowledge is imperative if step change improvements in absorption-based separations are to be realized. Further, the evidence suggests that this step change is truly attainable, bringing practical, large-scale carbon capture and separation much closer to reality. The basic questions addressed are not limited to this domain, however. Similar questions emerge in membrane- and adsorbent-based separations, of course. But gas–liquid interactions are also central to biology, to environmental and atmospheric chemistry, to catalysis, to chemical processing, and even to sequestration. The knowledge and associated computational and experimental tools will advance fundamental scientific understanding and ultimately capability in all these domains.

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PROCESS CONCEPTS DISCOVERY

Abstract

Current methods for carbon capture, based primarily on the use of liquid solvents such as amines to scrub carbon dioxide from postcombustion flue gas, have cost estimates in the range of \$20/t CO_2 *to nearly \$100/t* CO_2*.*[1,2] *These are low-end estimates, since they represent operating costs only. Such costs are not acceptable economically, since they would potentially double the cost of electricity, reflecting the power lost to carbon capture and sequestration activities, and thus put US industry in an even less competitive position than it currently is. Thus fundamentally new, low-cost, low-energy methods for carbon capture must be identified, with more acceptable economics. This requires the development of the fundamental understanding and the methodologies needed to enable exploration of novel process concepts—that is, designing separations from a systems perspective. One of the fundamental limitations to process concept exploration and discovery is the lack of robust, accurate theoretical methods to predict the physical, chemical, and kinetic properties needed as input to process calculations. Thus we require the development of these methods by combining first principles and molecular approaches, through the derivation of new theory, and by their implementation on state-of-the-art computing platforms.*

Background and Motivation

The development of a traditional solvent process in the processing industry—particularly the chemical industry—is a relatively mature process. Figure 14 illustrates the methodology used by process developers to develop liquid-solvent-based separations processes. Methods are well established for designing standard temperature- or pressure-swing absorption separation processes when the physical and chemical properties of the absorbent are well known. However, it is essentially impossible to apply them to novel carbon capture processes for lack of a robust theoretical capability to predict the physical, chemical, and kinetic properties of absorbents under realistic separation conditions. Engineering models of new absorbents and new separation methods require knowledge of a myriad of physical, chemical, and kinetic properties over the wide range of operating temperature, pressure, composition, and other conditions. To accelerate both the evaluation and the application of new absorbents, we require robust, accurate, atom-/molecule-specific theoretical methodologies for representing and predicting physical, chemical, and kinetic properties, as mentioned in the PRD "Interfacial Processes and Kinetics."

The traditional chemical engineering approaches for estimating such properties are based on the concept of group contributions. A mixture of molecules can be regarded as a mixture of the molecular groups within the molecules when the connectivity of individual molecules is taken into account (i.e., which molecular groups belong to which molecules). This concept also underlies molecular simulation: molecular dynamics (MD) and Monte Carlo (MC) simulations are performed using models for the interactions between atoms. These models are described by force fields, which are expressions for the energy of a system of molecules that include terms for repulsive, attractive, electrostatic, bond-stretch, bond-angle-bending, and torsional interactions. More sophisticated models also include polarizability. The concept of transferable force fields (which underpins all the biological and most physical and chemical MD and MC simulations performed today) is that once the interaction between, for example, a methyl group and a hydroxyl group is determined, it can be used (transferred for use) in simulations of other mixtures. General force fields based on this concept include

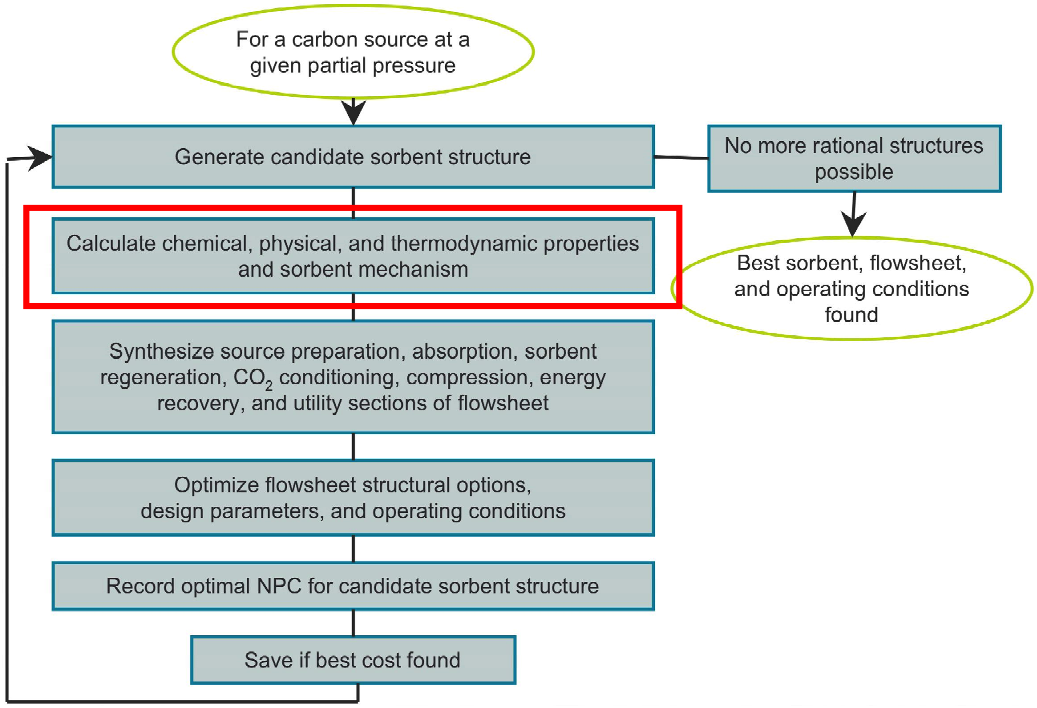


Figure 14. Systematic methodology for developing optimal liquid-solvent separation processes. This includes the "structure" of the process—represented by a "flowsheet"—that lays out how inputs to the process inputs, intermediate streams, and process outputs are connected to and by "unit operations," such as separation columns, pumps, and compressors. An optimized process is one in which the cost-optimal structure is identified, as well as optimal values of all stream properties and unit operation conditions. The key scientific impediment to routine application of this methodology, particularly to invent new processes, is the absence of methods to predict robustly and accurately the physical, chemical, and kinetic properties of fluids and materials of arbitrary complexity and composition (see the red box). Courtesy of J. Siirola, Eastman Chemical.

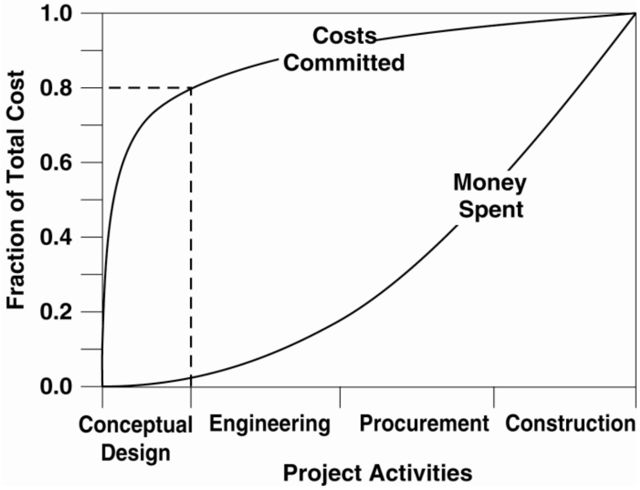
CHARMM, AMBER, OPLS, TraPPE-UA, and TraPPE-AA. Force fields are developed by fitting to ab initio (first principles quantum) calculations and to experiment. However, as the sophistication and accuracy of first principles methods increases over time, along with the availability of the required large computational resources, force fields are increasingly determined exclusively by fitting to ab initio methods. The problem with engineering correlations for thermodynamic properties (such as UNIQUAC/UNIFAC for activity coefficients) is that the group contribution concept—which, as we see, is equivalent to the assumption of transferability in force fields—is applied using a model for thermodynamic properties (e.g., activity coefficients) that is too simplistic.

UNIQUAC/UNIFAC and similar properties correlations revolutionized the chemical industry's ability to conceptualize new processes in which the chemical natures of the fluids became variables; however, UNIQUAC/UNIFAC is based on regressing group–group contributions from *experimental* data, which over limited ranges of conditions compensate for the simplistic nature of the underlying activity coefficient model. Conceptualizing new carbon capture processes requires a completely new approach in which properties prediction is based on modern molecular theory and simulation methods, since experimental data for the vast majority of candidate solvent systems are not going to be available, either for direct use or for regression of parameters.

The urgency of conceptualizing new carbon capture processes is illustrated in the sidebar "The Lessons from Engineering Design": the more concepts for carbon capture we can explore early, the higher the probability that more cost-effective carbon capture processes will be discovered, and that the eventual cost of carbon capture can be significantly reduced. The discovery process is strongly impacted by and interleaved with experiment, since many of the innovations in new solvents originate from insights from experimental studies.

The Lessons from Engineering Design

The accumulated experience of decades of engineering project management shows that early consideration of the widest possible range of designs is crucial to minimizing costs in the long term. As illustrated at right, in any major engineering project—such as designing a chemical plant, a building, a bridge, an aircraft, or a car—the conceptual design stage is when costs are committed and locked in. Once a conceptual design is determined, it is optimized (engineering), and the procurement and construction stages begin; it is during these latter stages that most of the money is expended. Changing the conceptual design at this late stage is extraordinarily costly, and the engineering literature is filled with examples of order-of-magnitude or more cost overruns when conceptual designs are changed later in the process. The lesson for carbon capture is that we must consider the different possible scenarios for carbon capture as early as possible, and this in turn requires unprecedented predictive capabilities.



Courtesy of M. Malone, University of Massachusetts.

Research Directions

New computational tools for modeling intermolecular interactions in complex environments

The rise of molecular simulation and first principles methods in recent decades has benefited from two trends. First, the exponential increase in computing power driven by Moore's law has increased computer speed by three orders of magnitude per decade at the high end (the top 500 supercomputers in the world, updated twice yearly at www.top500.org). The result is that the first scientific calculations to achieve 1 petaflop (10^{15} floating point operations per second, or FLOPS) have been reported in the past two years. There is every indication that this trend will continue, with exaflop computing (10^{18} FLOPS) expected around 2018, although achieving high levels of computational efficiency will be challenged by the emergence of multicore chips. We have entered an era in which Moore's law is achieved by doubling the number of cores in each microprocessor chip, rather than increasing clock speed, adding another level of complexity to the programming model for scientific computing. Second, the community of materials simulations scholars is constantly innovating, so new algorithms often result in multiple-orders-of-magnitude speed increases without any change in hardware. Examples abound, particularly in MC methods for classical simulation (such as multispin methods for Ising systems and continuum configuration bias methods for complex molecules). There are new $O(N)$ methods for first principles calculations in which the cost of the computation scales linearly with the number of electrons, N, rather than by the nonlinear $N^3 - N^7$ scaling of current methods.

The combination of algorithmic and hardware advances will result in first principles and molecular simulation computations becoming far more routine. *De novo* predictions of the properties of a proposed new solvent require first principles methods to obtain gas phase properties, calibrate classical force fields, and model chemical reactions, and classical molecular simulations to obtain condensed-phase properties. (First principles methods include quantum chemistry methods; density functional theory [DFT]; and ab initio molecular dynamics, in which the classical equations of motion for atoms are solved using forces calculated on the fly from quantum chemistry or DFT methods.) Several methods exist for automated fitting of classical force fields to first principles calculations, but currently they are not widely practiced. To develop the capability of providing the key physical and chemical properties needed for novel carbon capture process design, a suite of molecular modeling tools based on state-of-the-art first principles and molecular simulation tools is required. A partnership between end-users of the predicted properties (process design researchers) and the molecular modeling community is needed to identify the properties required. In addition, a mechanism is needed to ensure computed properties are made available in standards-compliant properties databases used by process designers.

New molecular theory for novel solvent design

Continuing improvements in theory, algorithms, and computing hardware speed are resulting in computationally intensive methods (e.g., quantum chemistry and molecular simulation) that provide routes to key physical and chemical properties considered equal in accuracy and precision to experimental measurements. For example, in gas phase thermochemistry, many companies moved from experiment to computational quantum chemistry methods more than a decade ago to obtain free energies of formation and reaction.[3] The reason is that quantum chemistry methods provide equivalent or higher accuracy at much lower cost. Developing the computational molecular-based approach to properties prediction that was described earlier will result in a large properties database for novel solvent systems and the capability of adding to it in ways that directly provide data for group contributions. Thus the opportunity exists to create a new, molecular-based *theoretical* approach to physical properties prediction to replace the current engineering group-contribution methods. The idea of using modern equations of state based on molecular theory (such as variants of the statistical associating fluid theory and other statistical-mechanics-based approaches) in a group-contribution context is in its infancy. Such approaches—because they are based on molecular models for the molecules involved that parallel intermolecular force fields—are a promising route to analytic formulae for condensed-phase thermophysical and chemical properties that accurately reflect the chemistry and structure of the constituents of mixtures. Analytic formulae are crucial for repeated calculation of properties needed in process *optimization*; additionally, because analytic formulae can be evaluated many orders of magnitude faster than molecular computational approaches, they make molecular design feasible. That is, rather than beginning with a candidate system and calculating properties, one can begin with the desired properties and find the system(s) that will give them, yielding a molecular design capability for new solvents.

Scientific Questions and Opportunities

The drive toward the successful development of computational and theoretical molecular-based approaches to properties prediction will have significant impact on several scientific fields. It will require the development of new theory (e.g., new DFTs that accurately describe the particular systems of relevance in carbon capture, new methods for connecting the electronic and atomistic scales, new statistical mechanics theory for computing condensed phase properties analytically) as well as new algorithms leading to efficient computation on exascale computing platforms, multicore chips, and novel architectures such as graphic processing units (GPUs). We are at the beginning of the GPU and multicore revolution, but already speed increases of factors of 20–80 are being reported for quantum chemistry and molecular simulation codes on GPUs. GPUs and multicore chips are creating the potential for a truly revolutionary change in the level of computing available to the research community, and hence the utility and ubiquity of computational approaches, but researchers must learn how to use them effectively. Today, most of the best minds engaged in computational chemistry are focused on biology; refocusing the efforts of the best computational and theoretical researchers on chemical systems will have a dramatic impact on the field of chemistry in general, and energy-relevant chemistry in particular.

Potential Impact

Successful development of computational and theoretical molecular-based approaches to properties prediction will revolutionize the ability to conceive of novel solvent-based separations for carbon capture. Indeed, the frameworks proposed will result in the creation of true integrated product–process design for carbon capture. Extending this approach to other chemistries and processes will revolutionize all of the processing industries at a time when many processes need reinvention to take into account the rapid changes taking place in industry, such as likely future mandates to reduce or eliminate greenhouse gas emissions; increasing environmental regulation of waste; and feedstock changes from petroleum to coal, biomass, natural gas, or even carbon dioxide. Providing the scientific tools to enable U.S. industry to meet all of these changes is crucial to protecting the environment and making these industrial processes more efficient to keep jobs in the United States.

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DESIGN, SYNTHESIS, AND ASSEMBLY OF NOVEL MATERIAL ARCHITECTURES

Abstract

To meet the challenge of lowering carbon emissions from combustion processes, new sorbent materials are needed with specifically designed structures that allow them to selectively bind a targeted gas from a complex mixture and release it in a controlled fashion when triggered by external stimuli. Currently, there is a lack of fundamental understanding of gas uptake and release on the nanoscale, which has led to an Edisonian approach to material selection and optimization for gas separations. This lack of understanding continues to hamper the design and development of alternative solid sorbents with improved capacity and lower energy consumption in the sorption/desorption cycle. Armed with this knowledge however, it should be possible to discover and design new material architectures tailored on multiple length scales (molecular, nanoscale, mesoscale, and macroscopic) and incorporating multiple functional domains to further enhance performance. Achieving this goal will require strongly coordinated multiscale modeling, analytical characterization, and synthesis and assembly techniques to achieve new materials with controlled pore structures, tailored pore surface texture and functionality, and nanoscale architecture, all of which will be required for future carbon capture technologies.

Background and Motivation

Solid sorbents currently used for gas capture include zeolites, activated carbons, calcium oxide, and alkaline and alkaline-earth hydrotalcites.[1] More recently, additional materials—including amine-enriched solids, metal-organic-frameworks (MOFs), lithium zirconates, and other natural and synthetic materials—have been explored as potential gas capture materials (Figure 15). Some MOFs have been shown to possess well-defined pore structures and surface areas in excess of 3000 m^2/gm and have demonstrated impressive gravimetric uptake.[2]

However, no material available to date is able to satisfy all the requirements of future carbon capture processes. Furthermore, most of the studies on these materials were done using trial-and-error tests (e.g., testing dozens of commercially available activated carbons). This Edisonian approach cannot provide greatly needed guidance on how to design better solid sorbents; only a fundamental understanding of the sorption mechanisms that occur at the atomic and molecular level will provide the basis for the development of next-generation sorption materials. With this understanding, new strategies for formulating optimized architectures and functionalities can be translated into revolutionary new materials for improved gas uptake and release.

Science Research Directions

Understanding of the physical and chemical parameters governing solid sorption is a prerequisite for increasing the volumetric and gravimetric uptake of CO_2 and other targeted gases associated with carbon emission mitigation. This insight will enable new sorption, transport, and desorption mechanisms that will dramatically increase carbon capture schemes. In designing new sorption materials, one must consider the use of larger pores (tens of nanometers) to facilitate fast transport and gas/surface interactions, and even perhaps tunable nanopores to facilitate both uptake and release of targeted gases. Therefore, research must be directed toward understanding multiple sorption mechanisms that occur at the atomic and molecular level. Once these processes are understood, using new characterization techniques combined with computational modeling, the challenge will lie in the synthesis of these new materials.

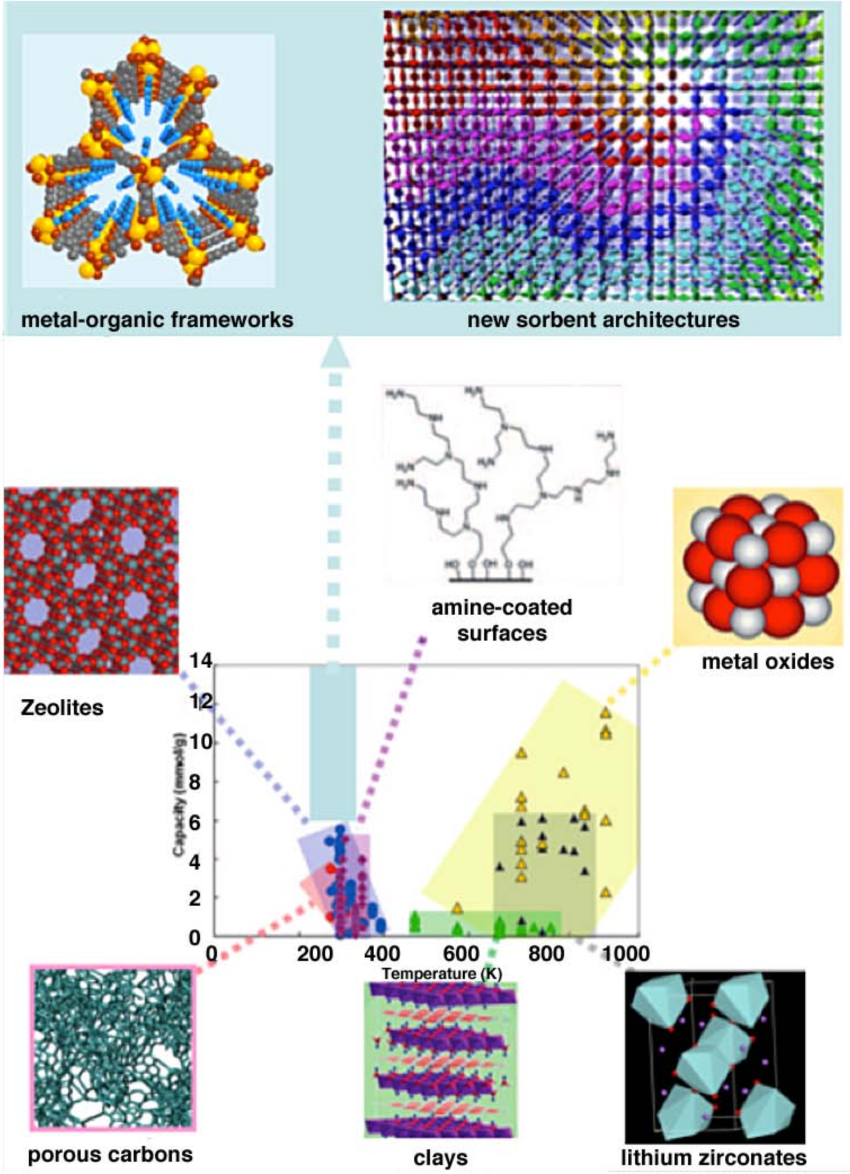


Figure 15. Currently used and researched sorbents and their capacity as a function of temperature. *Source:* Refs 2, 3, and 4.

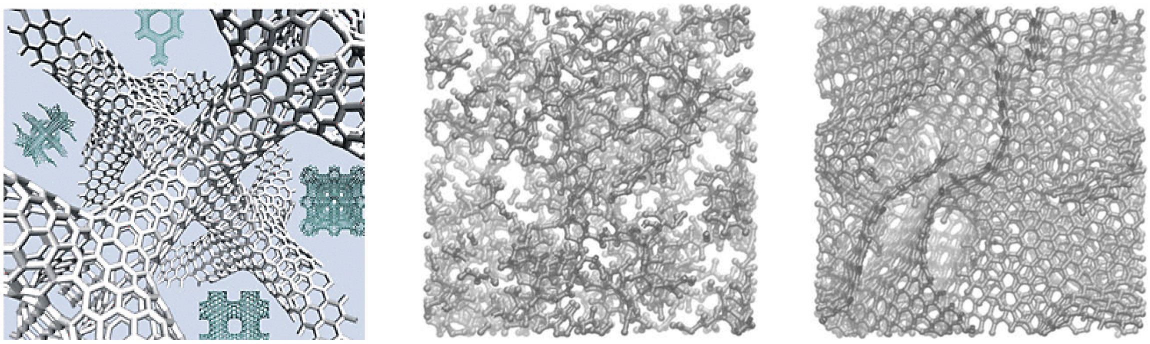
The sorption properties of nanostructured materials rely on hierarchical structures at three discrete length scales. The first length scale involves the molecular-level structure constituting adsorption sites and their immediate surrounding environments.[5] The interfacial functionalities of the adsorption sites can be tailored for carbon capture through surface modification, doping, and topology. The second length scale is in the range of nanometers and corresponds to the structures of mesopores (2–50 nm in diameter). The mesopores not only provide access to micropores but also furnish hosts for creating unique confined sorption sites through surface functionalization. Rational synthesis of porous materials with controlled pore sizes[6] and controlled morphologies is the key to enhancing selectivities for well-defined nanostructures. The third length scale, in the micrometer range, plays important roles in determining the efficiency of mass transport (CO_2 flow rate).

The accessibility of deeply embedded adsorption sites depends on the macrostructure. Multimodal porous materials with a controlled macroporosity that incorporates mesoporosity and microporosity represent one strategy for achieving the maximum utilization of sorption sites at different length scales. Efficient carbon-capture systems hinge on the synergistic interplay of the hierarchical structures related to the three different length scales. Accordingly, hierarchical synthesis methodologies based on self-assembly are needed to generate capture sites and, ultimately, integrated sorption media.[7] Nature has provided an ample number of examples of hierarchal materials that possess precision molecular recognition. The key synthesis strategy underlying the manufacturing of active sites in nature is the "key-and-lock" principle of templating synthesis and compartmentalization. In this context, various 0D, 1D, 2D, and 3D nanostructures can be envisioned for efficient target gas separation.

As described previously, recent advances in the synthesis of complex materials, such as MOFs and mesoporous materials, have allowed pore sizes of solid sorbents to be more precisely controlled. Additional attention must be given to tailoring these pores for improved uptake and release of targeted molecules and ions. Further, entirely new classes of molecules are needed to expand the range of architectures that can be accessed. Beyond conventional materials with rigid structures like zeolites or standard activated carbons, the potential exists to identify new materials that use wholly new processes for controlled uptake and release of targeted gases. The understanding of those phenomena, as well as dimensional changes in porous or solid monolithic (e.g., polymer) structures caused by gas uptake or release, will allow the design of new materials with the required architectures. Such materials might incorporate switchable or flexible internal structures to accommodate large amounts of CO_2 without a drastic change in the macroscopic size/shape, which usually leads to material degradation. For example, there is a rich opportunity to explore designer structures whose porosity might equal or exceed that of currently known porous materials [Figure 16(a)].

One fundamental question that must be answered is what is the best pore size and shape for the highest CO_2 uptake. The answer will require reexamining our current understanding of CO_2 sorption mechanisms as applied on the sub-nanoscale level and learning the limits of how far this phenomenon can be extended. The experimental results will have to be coupled with new modeling approaches that specifically consider the interaction of solids with CO_2 and the properties (and eventually new ordered structures) of CO_2 confined in nanoscale pores.

Materials with monodisperse pore size distribution may be very important in future gas sorption schemes, be they oxide, carbon-based, organic, or otherwise. Unfortunately, the availability of such materials is currently limited. Today, high-surface-area activated carbons are prepared using a top-down approach employing chemical or physical activation, but this leads to random pore sizes and distributions. New synthesis routes, most likely incorporating a bottom-up strategy, are needed to achieve tailored-pore-size materials from a variety of materials families. Carbide-derived carbon materials offer a starting point for these studies [Figures 16(b) and 16(c)]. In these materials, the pore size is programmed through the carbide precursor structure and the surface chemistry is determined by the process conditions.[6]



(a) Nanotube networks

(b) Carbon-derived carbons produced at 600°C

(c) Carbon-derived carbons produced at 1200°C

Figure 16. Atomic simulation of 3D ordered architectures (a) and disordered architectures (b) and (c). *Source*: Refs. 4 and 7.

Additional sorption specificity may be achieved by modifying the surface of a sorbent—either on a particle or in a pore. If specific functional groups are added to a structure, enhanced sorption and release mechanisms can be employed, including those that use external release triggers, such as applied fields. Beyond simple porous materials, many types of "designer structures" could be imagined to enhance sorption/release processes. For example, it has been demonstrated recently that combining the inherent rigidity of MOFs and the functional flexibility of polymers can create a large number of single-phase materials, each of which has multivariate functionalities (Figure 17). The properties of multivariate MOFs are not simple linear combinations of their constituents; this supports the notion that the sequence of functionalities within a porous network may well be useful as code for enhancing a specific property or achieving a new property.[8]

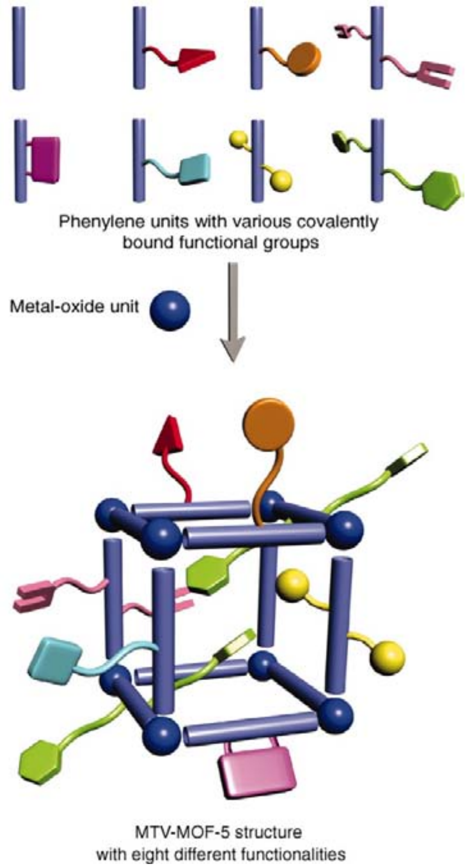


Figure 17. Multivariate MOF-5 structure with eight different functionalities. *Source*: Ref. 8.

Another approach to increasing the selectivity of solid sorption separation is to introduce coatings to sorbent materials by depositing a continuous, thin, conformal coating onto high-specific-surface-area substrates. For example, introducing metal or oxide nanoparticles and clusters with terminal functionality to a sorbent in a controlled manner has the potential to control CO_2 sorption. Again, the goal is to enhance the uptake and control the release of a targeted gas, taking advantage of various processes such as using external stimuli to affect release, decreasing the activation energy, and modulating the heat of adsorption. For example, one might consider coating a material that incorporates iron or nickel oxide onto carbon to enable magnetic manipulation/triggering of the sorbent.

The discussion in this PRD is meant to inspire the development of wholly new concepts for solid sorbent materials. Such materials with improved structure and functionality will require the development of alternative synthesis routes guided by a fundamental understanding of chemical and physical processes involved in gas sorption/release.

Scientific Questions and Opportunities

- A key fundamental question revolves around the roles of pore structure and pore size for efficient sorbents. Answering it requires a rethinking of traditionally held views on effective sorbents. Can systems with a controlled pore size and structure be used as models to elucidate gas–solid interactions?
- Tailoring the surfaces of solid sorbents has enormous potential for improving gas uptake and release. Can the curvature of a particle be tuned to obtain reversible, high-specificity gas sorption? Can surface functionalities be incorporated on surfaces and in pores to enhance sorption and improve selectivity while maintaining long-term cyclability? Can heterostructures based on highly porous carbon, MOFs, polymers, and other porous networks provide another route to improved gas separation schemes?
- Advances in nanoscience and technology have provided new tools for synthesizing materials. Can nanoscience provide novel modalities of control over structure and properties to enhance gas uptake/release strategies? Can new classes of materials be synthesized by self-assembly or top-down approaches?

Potential Impact

Maximizing the density of gas sorption within the adsorbent volume, controlling the mechanisms and rates of adsorption and release, and developing new materials with higher selectivity will lead to drastically improved capacity and energy efficiency for targeted gas adsorption and desorption throughout the carbon cycle. Success in the discovery of new material architectures will require interdisciplinary teams to develop new sorbent architectures,which will involve close coupling of theory, synthesis, and characterization. Development of new solid sorbents with improved selectivities will have a broad impact in many areas beyond carbon capture, including gas purification and emission control processes used across industry. The new generation of complex nanostructured material architectures developed for targeted gas sorption may impact other energy-related applications, including catalysis, energy storage, and water desalination

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COOPERATIVE PHENOMENA FOR LOW NET ENTHALPY OF CYCLING

Abstract

Cooperative processes are those that can be accomplished by coupling the binding of a target gas with a change in a structure or other change in the sorbent material to lower the overall energy cost of the coupled uptake and release process. Taking advantage of cooperative phenomena has the potential to greatly enhance the thermal efficiency of gas sorption processes. To discover and exploit these cooperative phenomena, computational tools will be required to guide the discovery and design of a new generation of separation materials.

Background and Motivation

This PRD seeks to enhance the efficiency of reversible gas sorption by developing new materials systems that exploit the coupling of gas sorption with the underlying molecular structure of materials. The thesis of this concept is that the thermal efficiency of gas sorption (CO_2, in this case) can be significantly enhanced by coupling the gas binding process with a structural (or chemical) change in the material to which the gas binds so as to enhance thermal efficiency. In noncooperative binding, each sorbent-CO_2 binding interaction is thermodynamically downhill (exothermic); therefore, an energy cost is associated with subsequent release of the CO_2 from the sorbent, which adds to the overall cost of CO_2 capture and release. If the binding of CO_2 can be intimately coupled with another process that *requires* (endothermic) energy (e.g., a structural change in a molecule), the overall energy required for release of CO_2 will be diminished. The coupling of CO_2 binding with a change in the properties of the sorbent is what we mean by *cooperative* phenomena. This idea is inspired by examples in nature, for example, the reversible binding of oxygen to hemoglobin. This area of research has the potential to substantially lower the cost of CO_2 (or other gas) capture and release by reducing the parasitic heat cost of CO_2 release and by decreasing the price of oxygen production for oxycombustion and precombustion processes.

The types of changes that might occur in the sorbent material span a wide range of length scales, from the molecular to the macroscopic; and, indeed, different types of materials will exhibit changes at different length scales. Gas binding can, for example, induce subtle structural changes at the molecular scale in transition metal coordination compounds. On the other hand, the volume of highly porous materials can change by macroscopic amounts upon uptake of molecular species; an example is water incorporation into a sponge. Building on this concept, changes in the sorbent material that would lead to either uptake or release of gases could also be triggered by external stimuli, such as an applied voltage, or mechanical stresses that have a low energy cost compared with heating (see the PRD "Alternative Driving Forces and Stimuli-Responsive Materials for Carbon Capture").

Achieving this concept will require the discovery, synthesis, and assembly of new materials systems, along with characterization and modeling of these novel processes. Investigation of various materials that respond to the binding of CO_2, O_2, or other gases will provide fundamental information that will yield insight into how best to exploit this approach. It is possible that changes on a specific length scale will be optimal for achieving the goal of low net enthalpy for the overall process.

Successful integration of this concept into carbon emissions reduction technology also requires that the rates of uptake and release be rapid. Because the coupled materials changes will necessarily be energetically "uphill," the rates of gas uptake or release could be substantially reduced. Investigating the rates and the mechanisms of gas uptake and release in these systems will enable the development of a predictive framework for coupling materials changes with gas sorption. To fully understand these processes and to develop a rational approach to constructing cooperative systems, new experimental and theoretical methods are needed in conjunction with creative application of existing methods for synthesis, characterization, and modeling.

Research Directions

Creation of new materials with nonlinear responses to CO_2 or O_2 binding

There are four general approaches to the discovery and exploitation of cooperative effects that will result in an overall low enthalpy for capture and release of CO_2 or O_2. These approaches can be heuristically organized on the basis of the length-scale of the cooperative interaction: (a) atomically local, (b) molecularly local, (c) nanoscopically and microscopically confined, and (d) macroscopic.

(a) **Atomically local.** Inorganic molecular complexes illustrate that ligands coordinated to the metal center can affect one another's binding mode and binding energy. As a simple example, the stepwise dissociation of the four CO ligands from $Ni(CO)_4$ to give $Ni(CO)_3$, $Ni(CO)_2$, Ni(CO), and ultimately atomic nickel come with significantly different energy costs. The essential challenge faced in devising strategies for cooperative CO_2 capture is whether sorbents can be synthesized in which the local, active sites for CO_2 adsorption show similarly nonlinear effects.

(b) **Molecularly local.** There are examples in nature in which the binding of one molecule to an active site in a material increases its affinity for binding of a second molecule. Perhaps the best-known example is hemoglobin, in which the absorption of one molecule of O_2 to the previously completely deoxygenated substrate affects the thermodynamics and kinetics of the subsequent oxygen coordination steps. The mechanism of this amplification involves the structural reorganization of the substrate so that the coordination sites are mechanically optimized on the nanoscale for subsequent oxygenation (Figure 18). The materials challenge here is to invent analogous microenvironments for the cooperative absorption of multiple equivalents of CO_2 to the same "active area."

(c) **Confinement at the nanoscale or micron scale.** Three-dimensional environments can be designed and constructed that behave like gas sponges. One way to do this would be to prepare a material that has defined but flexible pores that can facilely expand or contract, but which robustly cycle their structures between the gas-filled or empty states. In an ideal case, the material would be mechanically bistable: one state would be gas-deficient and the other would be gas-rich. As ambient conditions changed (e.g., temperature, pressure) to move from one bistable extreme toward the other, the material's shape-memory would accelerate the influx and outflow to and from the pores. An example of such a material is nanoporous gold, which has been shown to expand and contract in response to uptake of gases (Figure 19).[1] Synthesis of materials for this type of reversible absorption, albeit with CO_2, will enable us to test the efficacy of changes on the nanoscale and micron-scale.

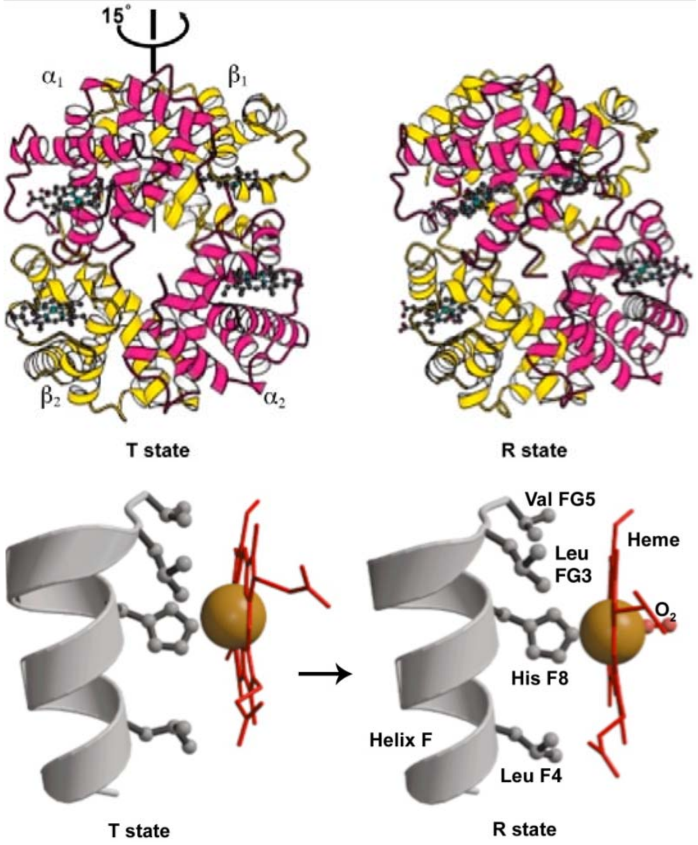

Figure 18. Top: Quaternary structures of deoxyhemoglobin (T state) and oxyhemoglobin (R state), which demonstrate considerable structural change upon uptake of an O_2 molecule. Bottom: Detail of changes in heme structure upon uptake of O_2. Note that in the T state the structure of heme is nonplanar, and in the R state, the heme structure is planar. (An animation of oxygen uptake by hemoglobin may be seen at http://www.biochem.arizona.edu/classes/bioc462/462a/NOTES/hemoglobin/oxy5.html.)

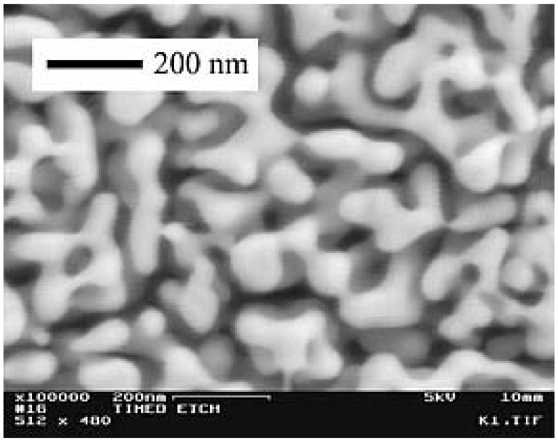

Figure 19. Scanning electron micrographs of nanoporous gold made by selective dissolution of silver from Ag-Au alloys immersed in nitric acid under free corrosion conditions. *Source:* J. Erlebacher, M. J. Aziz, A. Karma, N. Dimitrov, and K. Sieradzki, “Evolution of nanoporosity in dealloying,” *Nature* **410**, 450–453 (March 22, 2001).

(d) **Bulk effects.** Phase changes are the quintessential examples of cooperative phenomena, in which a material can be more strongly associated with one phase than another. The scientific challenge is to develop materials that can exist in two (or more) phases that possess dramatically different gas capacities. A critical requirement is that the targeted gas be vigorously absorbed or expelled when the material is coaxed from one phase to another by an external stimulus—such as heating, pressure variation, application of a voltage or magnetic field, or irradiation with light (see the PRD "Alternative Driving Forces and Stimuli-Responsive Materials for Carbon Capture").

(e) **Rates of gas uptake and release in cooperative systems.** Rapid uptake and release of gases, such as CO_2 and O_2, is a central requirement for their efficient capture and release; therefore, the kinetics for reversible gas sorption in these cooperative systems are as important as the low overall energy budget. Interfaces—between gases and solids and between different solids—are gating factors in determining the rate for any gas sorption process. In these cooperative systems, the energetically-uphill changes in the sorbent that are required to lower the overall energy cost may also severely decrease the rate of uptake. Generally, the speed of gas sorption will be determined by (1) the mechanisms of binding of gases to the external surfaces of the sorbents (adsorption), (2) transport of the sorbent into the bulk of the material (absorption), and (3) the mechanisms and energetics for coupling materials transformations to key the adsorption and absorption steps and their reverse (release).

Changes induced by binding of molecular gases can occur on different length scales, from the molecular to the macroscopic, as discussed earlier. Even if a change is energetically favored overall, though, there must be an accessible mechanistic pathway under the conditions of the reactor for that change to occur. A central challenge will be to determine which length scales lead to the fastest rates of sorption and release. There may be an optimal length scale over which the reorganization takes place in the material that leads to a fast rate of uptake (or release) and a low net energy cost. Theoretical models that can be applied self-consistently over a range of length scales will provide important insights into the interplay among kinetics, energetics, and length scale.

An exciting opportunity is to test the rapidity of sorption and release of CO_2 and oxygen using different types of stimulation. Typically, either temperature or pressure swings are used to release CO_2. Alternatively, electrical, magnetic, mechanical, or light stimulation might facilitate transformations that induce either uptake or release of gases (see the PRD "Alternative Driving Forces and Stimuli-Responsive Materials for Carbon Capture"). This approach has the potential for high reversibility with low energy input. The conceptual basis for this focus area is based on the fact that materials transformations are known to be triggered by external stimuli. For example, piezoelectric materials—a special class of metal oxides that expand or contract upon application of an external voltage—have recently been shown to have differential binding energies for CO_2 depending on the polarization of the surface.[3] This single result provides reason to believe that external stimuli other than heat and pressure changes could drive uptake or release of CO_2 and other gases.

Discovery and elucidation of new structure–function relationships in complex materials

Cooperative materials processes involving structural changes during a chemical change that helps drive a chemical process are of interest for carbon capture and transport. A thorough understanding of the structures and related energetics of the starting and resulting materials is crucially important. This thorough understanding of structure–property relationships will facilitate the modification and optimization of materials to achieve a workable carbon capture or separation system for use in a range of operating conditions.

Our challenge is to investigate structure–function relationships in complex materials with a focus on the discovery and elucidation of new compositionally driven structural changes. Concomitant with any structural or chemical change is a change in the underlying electronic structure. Together, these create the energy landscape for a chemical transformation. Of particular interest are structure–function relationships of materials that react reversibly with a target, such as metal-organic frameworks that bind target gases. Characterization tools are needed for local molecular-scale investigations of the atomic structures and energetics of binding events.

Key Scientific Questions and Challenges

Cooperative processes have enormous potential for increasing the selectivity and rate of gas absorption and release and could also significantly decrease the cost of the overall separation process. To achieve this vision, a number of scientific challenges must be addressed:

- What are the mechanisms for gas binding at the interface with a material?
- What materials transformations occur during the initial binding of the gas to the interface and how do they affect the energetics and the rate of this process?
- Can new materials be predicted and synthesized with tailored structures and functional groups to enhance cooperative phenomena?

To answer these questions, new experimental tools for measuring structure across various length scales—from molecular to macroscopic—are needed. These tools include methods for determining the kinetics and capacity for gas uptake, and visualization of bonds and of the structures of the sorbent materials. In addition, new multiscale computational methods are needed that can examine structure and bonding at the molecular scale and relate structure to chemical and physical properties from molecular scale to macroscales.

Scientific Impact

Processes that occur at interfaces are ubiquitous in separation processes, including carbon capture. However, little is currently known about these processes. Understanding the roles of interfaces—between gases and solid surfaces, surfaces and bulk, and different materials—has tremendous potential for establishing a new paradigm for facilitating uptake/release and mass transport of gaseous species in solid materials by exploiting cooperative effects. This knowledge will have impacts across a number of areas, including separations, catalysis, hydrogen storage, and other areas relevant to future energy processes.

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NOVEL HIERARCHICAL STRUCTURES IN MEMBRANES FOR CARBON CAPTURE

Abstract

New concepts inspired by nature are needed to produce novel membranes with hierarchical structures to optimize separations of targeted gases or ions. This will require new concepts for bottom-up self-assembly or top-down synthesis of materials into hierarchal structures of polymeric, inorganic, and even hybrid materials. New computational and characterization tools capable of application across broad spatial and temporal scales will also be required to support the development of these complex materials, allowing the prediction of the optimized materials structures. Such structures have huge potential for meeting future requirements for minimizing emissions of carbon dioxide from combustion streams and broad applicability in other areas of technology.

Background and Motivation

The creation of materials with controlled 3D hierarchical structure by rational design is critical to an increasing number of applications, including membrane separation, energy storage, electronics, catalysis, and sensing. For membrane applications, it is necessary to rapidly, scalably, and reproducibly generate such structures on multiple length scales (e.g., from nanometer to micron). Crafting such structures to function as highly efficient, robust membranes for carbon capture is extremely challenging. Further, highly efficient membrane structures require materials with graded free-volume architectures. Efficient strategies to predictably create such spatial heterogeneities in a single macroscopic construct are a grand challenge in materials science.

Hierarchical structures may offer novel ways of effecting low-energy membrane separations. Developing such new, broadly enabling forms of membranes, for use in carbon capture or in other processes, requires new approaches and significant fundamental advances in materials sythesis. The required advances span broad materials classes—including polymers, inorganic solids, composites, and fluids—as well as the ability to shape their structures and organizational architectures over length scales bridging the atomic/molecular level to macroscopic/continuum limits. Success requires the discovery and development of new capacities to harness specific chemical interactions, systems of chemistry, and transport dynamics. It requires new conceptual frameworks for design. It requires new, durable systems and synthesis and processing methods for constructing them. There also exists a critical opportunity to expand the design rules for membrane materials beyond traditional models. New architectures are required that combine enabling molecular features to prepare complex yet deterministically articulated 3D constructs. A grand challenge for research is to provide new materials that maximize selective mass transport through atomic/molecular architecture, structural dynamics, and physico-chemical phenomena.

Research Directions

Self-assembly. A natural question is to ask what *self-assembly*, biology’s main manufacturing tool, could offer to the development of these fabrication strategies. The current scientific platform of self-assembly is mainly centered on designed molecules that create nanostructures driven by noncovalent interactions. Departing from this relatively simple though not completely developed platform has been slow, since making the transition

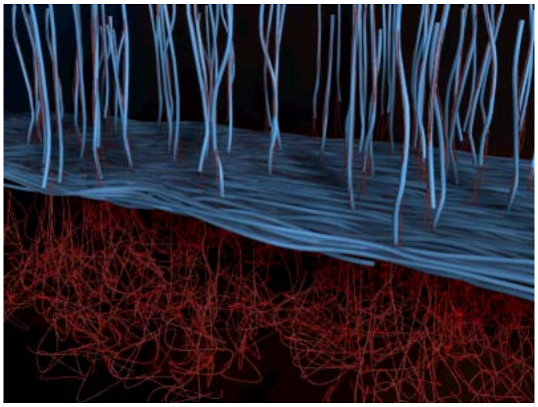

Figure 20. A hierarchical membrane formed from molecular constituents via a self-directed assembly process.

from nanostructures to hierarchical macroscopic constructs with self-assembly requires dynamic processes that trigger a sequence of physical events that build the structure. One might describe this process as pathway-dependent self-assembly, which is very likely to occur far from equilibrium. The example in Figure 20 shows molecules that assemble into a bilayer nanoscale membrane with two domains—one amorphous and one ordered—separating two liquids, leading to osmotic events that build, through diffusion, third and fourth layers with drastically different permeabilities. Permeability and mechanical behavior not only differ in the various compartments of this hierarchical membrane but also change as a function of time as the membrane grows further from simple reagents. One additional level of complexity in this type of membrane structure is its decoration with functional groups that can catalyze or react with molecules in specific compartments.

The chemistry used in building this variety of hierarchical structures by self-assembly could combine both organic and inorganic chemistry to create new high-performance robust membranes. Creative work in this area of materials synthesis could easily integrate supramolecular nanostructures, covalent and supramolecular polymers, metal organic frameworks, and ceramic-like lattices. As we approach 2020, materials heterogeneous in both architecture and composition could offer surprising new ways to capture carbon.

Materials chemistry. Membranes provide a powerful and generally enabling means to effect separations in complex fluid streams and have qualities that make them attractive for use in carbon capture. High transport rates and capacities for selectivity—combined with scalability and chemical, mechanical, and thermal stability in the process environment—are key attributes supporting their use. There remain significant challenges in developing next-generation membranes for carbon capture and storage, nonetheless. If highly scalable hierarchical structures are to contribute to next-generation membranes, advances in materials chemistry are required that will allow precise construction of these heterogeneous architectures. Multilayer laminates or surface textures offer additional degrees of freedom to tailor properties of hierarchical membranes. Polymer segmental motions and chemical interactions could be exploited to mediate solubility or diffusivity. Ceramic composition could be tailored to influence thermal expansion, vacancy concentrations, and so on.

There is a significant need and opportunity to more fully develop the chemistry of membrane materials in ways that harness either chemical mechanisms or specific forms of interaction (e.g., facilitated transport) to influence permeation rates and selectivity. This work must deliver those capabilities within materials that are robust in application-specific conditions. Systems of interest include high-permeance materials that can catalyze specific, reversible CO_2 transformations in ways that can then be hierarchically exploited in a low-energy separation. Materials are needed that can facilitate transport via specific but easily reversible interactions. Materials harnessing facilitated *uptake, transport, and release* would provide a model that more closely follows membrane-mediated transport of small molecules in biological systems. To fully adopt this analogy within industrial membrane separation technology requires new capacities to precisely tailor molecular interactions in a hierarchy with dynamics (e.g., conformational) that are currently impossible in synthetic materials.

Hierarchical 3D organization. Using current membrane materials and processes, it is estimated that capturing 90% of the CO_2 from a 550 MW_e coal-fired power plant would require 1 million m^2 of membrane area.[1] The membrane "footprint" can be reduced by integrating membranes in forms beyond the 2D motifs of current technology, i.e., hollow fibers and spiral-wound flat films. Adopting more effective, space-saving 3D designs could markedly enhance the efficiency of membranes for carbon capture and storage. General methods for preparing such structures with broad compositional and molecular variability would transform systems-level capabilities. This challenge cannot be addressed by conventional forms of synthesis or processing. However, the effort would benefit from recent advances that exploit the synergies of top-down and bottom-up means of designing materials structures for function by assembly and new/emerging 3D microscale and nanoscale fabrication. Each has a useful and empowering role to play in the production of robust, thermally and chemically stable, high-performance membranes.

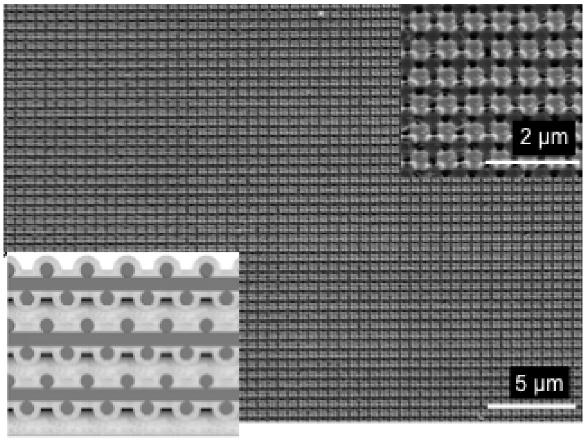

Figure 21. A bicontinuous mesoporous polymer monolith prepared by a large-area, low-cost phase-contrast lithography.

New patterning and fabrication methods allow novel, predictable 3D organization of materials. New phase-contrast and interference lithographies (Figure 21), as well as rapidly advancing methods of deterministic assembly and net-form direct-write fabrication, are promising ways of preparing complex integrated 3D architectures. There is a significant basic research opportunity in exploring new ways to prepare structures that are robust and highly scalable and offer previously unattainable property sets for membranes. Because the gas molecules of interest are of the order of a few angstrom, and CO_2 molecules differ from other molecules found in flue gas by only fractions of an angstrom, it is imperative that new techniques provide material structures that can effectively separate such mixtures of gas molecules. Specific opportunities include 3D organizations embedding gradient systems (e.g., density or composition), hierarchically porous materials, and asymmetric and/or heterogeneously integrated polymer networks. Constructing such systems is a frontier experimental challenge, and developing computational methods for optimizing the properties of such materials requires significant progress in topological mathematics.

Scientific Questions and Opportunities

The ability to design and synthesize hierarchical structures in membranes offers immense opportunities for efficient carbon capture processes. In biology, many of the most effective membrane-mediated separation/transport processes involve complex, nonplanar articulations of structure that are highly optimized to support function. Today, self assembly of materials is in its infancy and is relatively primitive compared with the structures found in nature. Achieving levels of sophistication similar to those seen in nature is a grand challenge in materials synthesis and would have huge impacts in broad areas of technology.

To meet this challenge would require the development of new concepts for effective self-assembly of materials. This would include expanding the range of materials to which pathway-dependent self-assembly can be applied. Ultimately, these concepts would establish self-assembly as a broadly enabling platform for functional materials design. Also needed is the ability to design and synthesize materials that have structure and function in three dimensions. Current approaches to making 3D materials through nanoscale and microscale fabrication are generally complex and limited in terms of the types of materials to which they can be applied, as well as potential structures and functionalities. New concepts are needed to revolutionize capabilities for producing 3D materials with tailored structures and functionalities that can provide both high permeability and efficient separations. Further, new concepts are needed that would facilitate incorporation of these 3D materials into more complex architectures, essentially building a “device-level” system for carbon capture processes.

Meeting these challenges will require understanding the dynamics of the assembly of materials from the atomic/molecular scale to the mesoscale. New computational tools are needed that can predict structures with functionalities optimized for selectivity and efficiency of separations in three dimensions . In addition, to fully understand, predict, and control the dynamics of self-assembly of these complex structures will require both new computational and characterization tools that encompass capabilities from atomic/molecular scales to the mesoscale.

Potential Impact

Multifunctional hierarchical structures generated by self-assembly could provide new routes to rapid fabrication of scalable, robust, high-performance membranes from polymer, inorganic, and hybrid materials systems. Beyond CO_2 capture, these advanced membranes could find application in purification of hydrogen for use in fuel cells or in membrane separators used in fuel cells and batteries. Further, membranes based on these revolutionary new structures could offer huge energy savings in commercial separation processes that typically use distillation, such as separation of water in bioethanol process. These advanced architectures may also impact other energy-related technologies, such as solar cells or photocatalkytic cells for fuel production.

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MEMBRANES MOLECULARLY TAILORED TO ENHANCE SEPARATION PERFORMANCE

New materials are critical for developing membranes of unprecedented efficiency to enrich CO_2 *or* O_2 *from complex gas mixtures for various carbon reduction strategies. New materials must be designed with specific functionalities to yield high specificity for the transport of target molecules or ions, or with catalytic properties for enhancing transport or selectivity. In addition, new membrane chemistries are needed to create more stable membranes than those currently used in gas separations. To achieve this vision, the chemical and physical mechanisms that affect membrane transport/separation properties and stability must be understood from the molecular to the macroscopic level. Doing so requires a new approach combining synthesis of membranes with tailored properties—guided by in situ characterization of chemical and physical interactions that affect separation processes and membrane stability—with advanced computational tools to predict and simulate those processes. The improved understanding of chemical and physical mechanisms is a critical underpinning for the development of next-generation separation processes with broad applicability to* CO_2 *capture and many other energy-related applications.*

Background and Motivation

New approaches to carbon capture using membranes require novel inorganic or polymer materials with high specificity for the transport of target molecules (i.e., CO_2, O_2) or ions (see Figure 22). Membranes incorporating species with specific catalytic properties in the bulk phase or surface of the membrane are another mechanism by which separations could be enhanced. This PRD focuses on new materials that will open opportunities for developing membranes with unprecedented efficiency for use in CO_2 reduction processes.

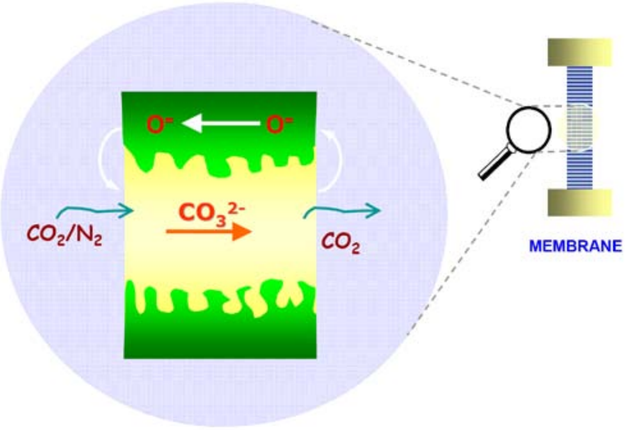

Figure 22. Concept of a CO_2-permeable composite membrane that incorporates interactions between carbonate and oxygen ions with membrane material.

Research Directions

One approach to creating membranes with high specificity for transport of target molecules is to design and synthesize them to incorporate specific interactions between transport species and membrane material. For example, facilitated transport has been widely studied for both liquid membranes and biological systems.[1] Incorporation of a reversible interaction into the membrane functionality has the potential to enhance both permeability and selectivity. Developing a fundamental understanding of how to **design and control** selective interactions will be critically important in designing revolutionary materials for use in robust, high-flux, high-selectivity membranes. Additionally, tailoring the structures of inorganic or polymer membranes could result in materials with greatly enhanced transport property profiles (see the PRD “Novel Hierarchical Structures in Membranes for Carbon Capture”). Such tailored membranes could achieve exquisitely high selectivity by using multiple strategies for sorting gas molecules or ions based on their interactions with the membrane.

An example of a recently described membrane that selectively transports CO_2 is a dual-phase membrane with one phase transporting carbonate ion and another phase, oxygen ion.[2] Carbon dioxide can permeate through the membrane under a CO_2 pressure gradient or an electrical field gradient. Carbon dioxide on the upstream membrane surface binds with an oxygen ion, becoming a carbonate ion, which is transported through one phase of the membrane. A reverse reaction on the downstream surface converts carbonate ions to oxygen ions and molecular CO_2, which is released at the downstream surface. An oxygen ion transporting phase, shown in green in Figure 22, moves the oxygen ion from the downstream to the upstream surface of the membrane so that it can again transport a molecule of CO_2 across the membrane. The result is a membrane with high specificity for transport of CO_2.

Membranes with high specificity for transport of target molecules may also be realized through the development of multicomponent composite membranes tailoredfor the synergistic enhancement of performance. For example, stable complexing agents that can selectively separate O_2 from air could be incorporated into membranes to provide a membrane with high permeability and selectivity for O_2. These complexes could take the form of a hemoglobin analog or a synthetic chelator that would selectively trap and release the target gas molecule or ion. Another example is a novel multicomponent membrane with high selectivity and permeability for a target gas, as shown in Figure 23. This concept is inspired by natural processes in which materials pass through a cell membrane via selective channels. The membrane has a composite structure with highly permeable carbon nanotubes as the support, and a polymer filling matrix optimized for chemical, mechanical, and thermal stability. The high perm-selectivity for CO_2 may be achieved through a specific interaction between CO_2 and tailored functionalities at the nanotube pore entrance.

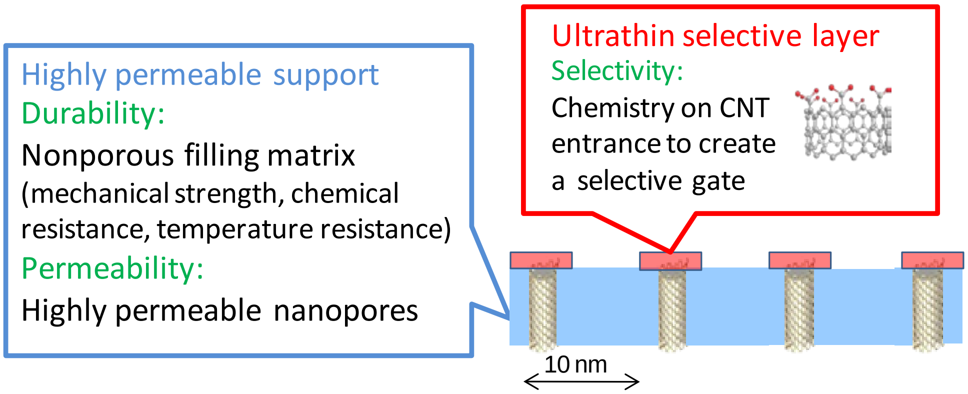

Figure 23. Concept of multicomponent membrane with durable high selectivity and permeance for CO_2.

Many existing membranes that selectively transport gases or ions have poor chemical, thermal, or mechanical stability. For example, perovskite-type ceramic ionic transport membranes offer high oxygen flux but suffer from surface contamination, bulk phase segregation, and/or mechanical rupture during operation, especially under large oxygen partial pressure gradients. Hydrogen-permeable ceramic or metal membranes also have severe surface contamination problems that cause a decline in permeation flux and a change in surface catalytic properties during use. Key chemical and physical mechanisms that affect membrane stability and transport properties need to be understood so that membranes with improved properties can be developed. New tools are required to study membranes at realistic conditions, allowing in-situ monitoring of chemical and physical properties of the bulk and surface of the membrane. Coupled with new capabilities for modeling these mechanisms, these tools could enable development of new membranes with vastly enhanced stability.

Scientific Questions and Opportunities

Polymeric materials that separate gases through the solution diffusion mechanism have dominated membrane technology for the past 30 years; however, new materials that take advantage of new transport mechanisms offer huge opportunities for significant advancements in technologies for efficient, cost-effective carbon capture. For example, facilitated transport and mixed ionic-electronic conducting ceramic membranes may achieve near infinite selectivity for targeted gases or ions by tuning chemical interactions with high specificity. Recent reports have demonstrated the efficacy of this approach for several challenging applications, including olefin/paraffin separations, oxygen and hydrogen purification, and CO_2 rejection. However, these materials (in the case of facilitated transport membranes) are often unstable or cannot operate efficiently at conditions relevant to those experienced in large-scale carbon capture (i.e., temperature, pressure, and gas composition). Therefore, significant fundamental advances in the design of new composite membranes are required to design membranes with high specificity for selective transport of target molecules relevant to carbon capture. Areas considered especially important include

- Understanding the roles of kinetics and nanoscale structure to enable the design of next-generation membranes that react reversibly with targeted molecular or ion species.
- New approaches for the synthesis of composite membranes that incorporate specific functionalities (e.g., chelators) to enable new modalities of efficient separation of targeted gases and ions using membrane technologies.
- Discovery of revolutionary new mechanisms not yet envisioned to selectively transport target molecules and ions across membranes.

Potential Impact

The research areas outlined in this PRD seek to obtain insight into material stability and specific membrane/gas interactions to design next-generation carbon-capture membranes with long life and outstanding transport performance. They also have the potential to make significant impacts on other fields such as fuel cell technology and membrane reactors. For example, the fundamental understanding and control of membrane material stability can foster the synthesis of novel, highly stable membranes and reveal synergistic material combinations that couple high transport rates with unprecedented selectivity. As a result, near-infinite selectivity and high permeance may be achieved at much lower temperatures than with current mixed-conducting membranes. Also, the ability to tailor chemical and physical interactions may enable stable membranes with exquisite selectivity for ionic and neutral species at the moderate temperatures typical of post-combustion flue gases. New insight into material properties, synergies between bulk and surface properties, and newly discovered pathways for property-driven design may inspire novel synthetic strategies. Finally, incorporation of functionalities with catalytic activity into membrane structures may provide alternative routes for fuel and/or flue gas conversion into useful products or benign byproducts. However, such materials will have value only if they exhibit stable properties and excellent separation characteristics at the conditions required for large-scale carbon capture.

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ALTERNATIVE DRIVING FORCES AND STIMULI-RESPONSIVE MATERIALS FOR CARBON CAPTURE

Abstract

Current gas separation processes typically use a chemical potential gradient IN the form of a change in pressure or temperature to drive capture/release cycles. For example, polymer membranes generally rely on pressure-driven transport, and ceramic ion transport membranes for oxygen separation rely on both thermal energy and partial pressure driving force. Indeed, nearly 35% of the energy produced in power generation can be consumed in these capture/release mechanisms. A major challenge in meeting future requirements for efficient carbon capture processes is to identify alternative driving forces that can be harnessed to achieve gas separation more energy-efficiently. These new driving forces could substantially lower the energy needed to achieve the desired separation.

Background and Motivation

Current gas separation processes are predominantly driven by a change (swing) in pressure or temperature, such as imposing a pressure drop across a membrane to concentrate the targeted gas or heating a solid or liquid sorbent to release the trapped gas. Creating temperature or pressure swings requires significant energy and accounts for much of the increased cost of electricity associated with current carbon capture processes, which are estimated to consume 30% or more of energy produced in power generation. Thus a fundamental challenge in improving carbon capture processes is to minimize the energy cost of driving gas (molecular or ionic) separation processes (see the sidebar "Novel Swing Mechanisms.")

This PRD focuses on the development of a new generation of smart materials to achieve low-energy isolation of targeted gases associated with combustion processes. In this PRD, both membranes and solid sorbent materials are considered, although similar processes could be incorporated with liquid sorbents as well. Materials that have switchable behavior could be triggered by a variety of possible mechanisms and could allow for an external stimulus to mediate the capture/release cycle in a facile manner. Dynamic materials are known,[1,2] including several highly porous materials such as metal-organic frameworks (MOFs).[3] One example is shown in Figure 24, in which an MOF lattice undergoes a phase change from a

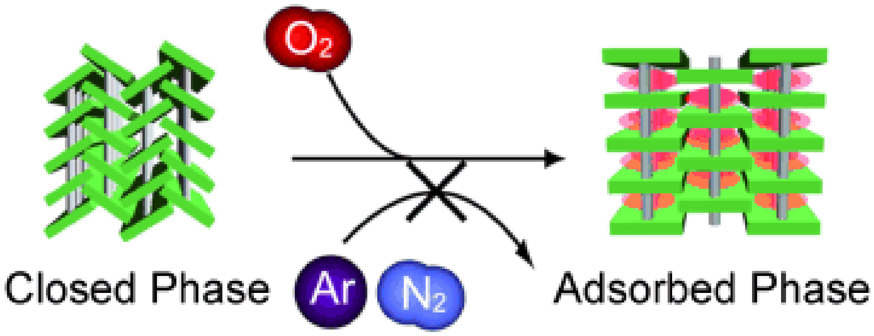
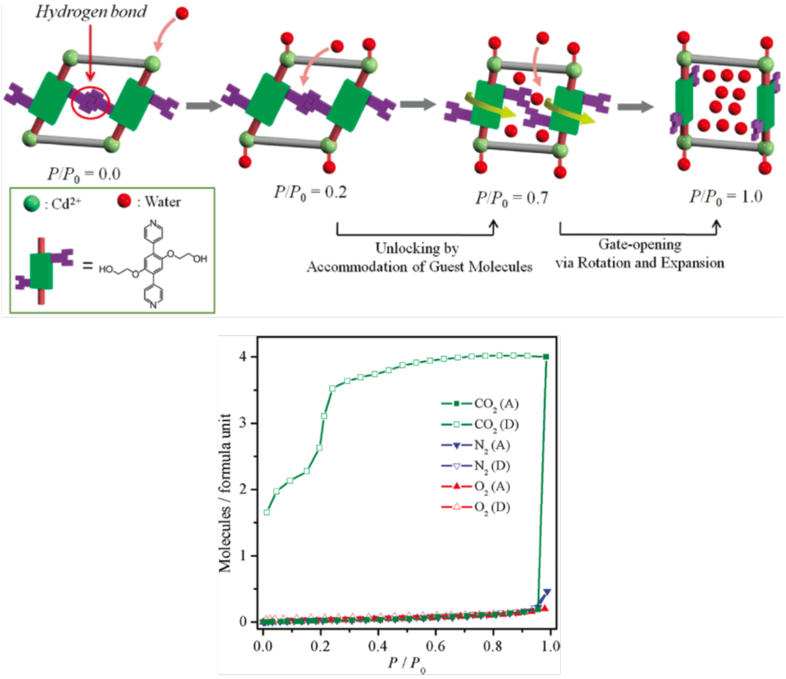


Figure 24. Guest-induced dynamic phase transition. Some MOF materials undergo large structural transformations upon guest binding. In this case, a low-porosity phase (left) transitions into a highly porous phase (right) in the presence of O_2, but not of Ar or N_2. *Source:* D. Tanaka, K. Nakagawa, M. Higuchi, S. Horike, Y. Kubota, T. C. Kobayashi, M. Takata, and S. Kitagawa, "Kinetic gate-opening process in a flexible porous coordination polymer," *Angew. Chem. Int. Ed.* 47, 3914–3918 (2008). Copyright Wiley-VCH Verlag GmbH and Company KGaA. Reproduced with permission.

Novel “Swing” Mechanisms

One major limitation of the existing technology for CO_2 capture from process gas is that it uses heat from power plant steam to remove the CO_2 from the sorbent. Such a process not only is energy-demanding, reducing the overall efficiency of a power plant, but also exposes the sorbent material to high temperatures over long periods of times, eventually resulting in their decomposition. Novel “swing” mechanisms that use different forms of low-energy inputs have the potential to significantly improve the overall efficiency of CO_2 capture. For example, an external stimulus can trigger a conformational change in the framework, thereby modifying the pore size and shape. This in turn lowers the affinity of the framework for the included guest, resulting in guest release. The stimulus input could be electrical, electromagnetic, electromechanical, magnetic, etc. In principle, such a mechanism not only may require less energy but also may be exploited to control the guest selectivity.

This concept of a new swing mechanism is schematically depicted in the figure, in which a flexible organic-inorganic framework material is shown reversibly changing its conformation in response to an energy stimulus.[4] Some of the organic constituents (shown as rods) are functionalized with side arms (shown in purple) acting as molecular gates that can switch between two states: locked and unlocked. In the locked state, the pores are inaccessible to guest (e.g., gas) molecules. Upon application of an external stimulus (in this case, water), the gates open, allowing the guest molecules (shown in red) to access the pores. In this particular system, selective adsorption of CO_2 over O_2 and N_2 is observed. The process can also be run in reverse, in which case the stimulus causes closing of the gates, thereby triggering the release of the guest molecules.



A flexible organic-inorganic framework material responding to an energy stimulus. Organic constituents (rods) have side arms (purple) that switch open to allow entry to guest molecules (red) when a stimulus is applied. *Source:* Ref. 4.

closed nonporous state to an open porous state upon gas binding. Note that this phase change is gas-specific, occurring only in the presence of O_2 and not of other gases, including Ar and N_2, suggesting that such systems could be appropriately tuned for selective CO_2 or O_2 capture.

Inspiration for new smart separation materials could perhaps be taken from nature. Biological cells take advantage of alternative driving forces such as pH gradients across membranes to drive protein and small molecule transport. Separation processes that use light-driven ion transport have been proposed,[5] as shown in Figure 25 in which a spiropyran-crown ether conjugate molecule enhances the diffusion of potassium ions across a membrane. Upon photoisomerization of the molecule to the less stable, more polar form, the molecule more easily travels to the ion-rich interface at which an ion is coordinated (i.e., captured) by the molecule. Then the molecule, which is coordinated with the ion, travels across the membrane and releases the ion at the other interface. Upon release of the ion, the molecule reverts to its original form, allowing the process to repeat. These examples provide exciting inspiration for identifying new driving forces for gas separations that can be harnessed with novel materials to reduce or remove the need for energy-intensive approaches to concentrating CO_2 from combustion streams, O_2 from air for oxycombustion, and other applications.

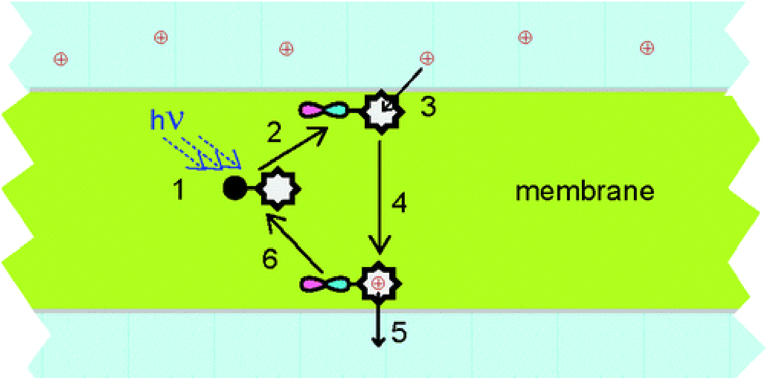


Figure 25. Scheme for light-driven transmembrane transport. Photoisomerization (1) converts the carrier molecule to a more mobile form that then relocates to the ion-rich interface (2), where the molecule binds with an ion (3), and travels across the membrane (4). The ion is then released at the opposite interface (5) before the carrier molecule returns to its original state (6), allowing the process to repeat. *Source*: R. F. Khairutdinov and J. K. Hurst, “Light-driven transmembrane ion transport by spiropyran–crown ether supramolecular assemblies,” *Langmuir* 20(5), 1781–1785 (2004).

Inspiration for smart materials can also be garnered from other fields of materials chemistry, such as controlled drug delivery. For example, light-driven molecular impellers have been designed within silicon mesopores to increase the pressure and flow of a fluid (Figure 26).[2] Stimulation by light causes the impellers to “wag,” thereby releasing the contents of the pores. Related systems have employed removable molecular caps on the exteriors of silica mesopores.[6] The general design principles of such smart materials might be considered for selective gas sorption and transport.

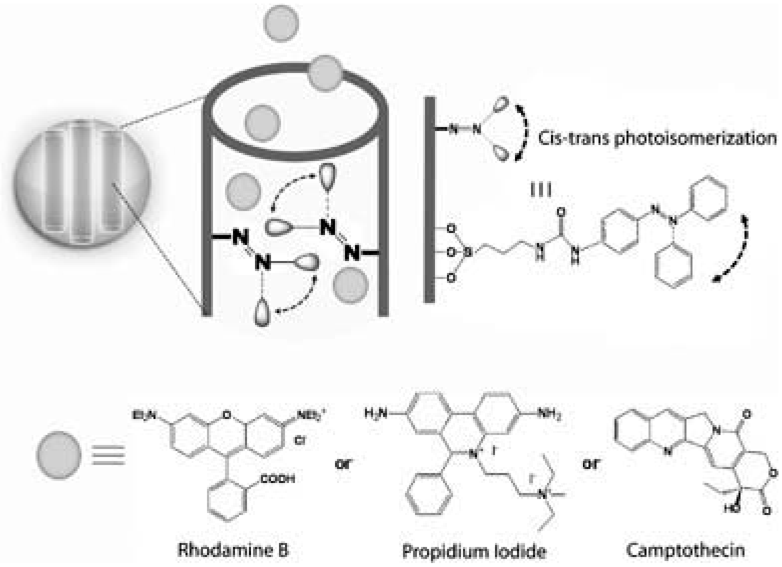


Figure 26. Light-driven molecular impellers: molecular rotors inside mesoporous silicon are used to generate fluid forces that can transport dye molecules through these narrow channels. *Source:* J. Lu, E. Choi, F. Tamanoi, and J. I. Zink, "Light-activated nanoimpeller-controlled drug release in cancer cells," *Small* **4**(4*)* 421–426 (2008). Copyright Wiley-VCH Verlag GmbH and Company KGaA. Reproduced with permission.

These examples provide a strong motivation for exploring the potential of designing a new generation of materials for membranes, solid adsorbents, and liquid absorbents that could greatly reduce the cost associated with carbon capture processes. These next-generation materials will be realized only with the capability to develop new materials with tailored structures and functionalities that respond to specific stimuli. Developing this capability will require a fundamental understanding of the interactions of applied stimuli with materials, and of the associated physical and chemical interactions of a targeted gas molecule/ion with the new materials, both with and without the effect of the applied stimulus. Advanced characterization and modeling tools are required to guide the synthesis and discovery of new materials and mechanisms that can be incorporated into revolutionary processes for efficient gas separation.

Research Directions

New classes of gas separation materials are needed that can harness driving forces (stimuli) to cause efficient separation of a targeted gas molecule or ion from a complex mixture. Smart materials that can be switched between capture and release conditions encompass a wide range of systems in which the stimulus causes a strong alteration of the chemical or physical interactions of the material with the target species (see the PRD "Cooperative Phenomena for Low Net Enthalpy of Cycling"). Such switching needs to result in a sufficient change in the binding affinity or capacity for targeted species without requiring a large energy input. Outlined in the following paragraphs are examples intended to inspire new approaches to designing materials or processes that would dramatically reduce the energy requirement for targeted gas capture and release.

Electrical or electrochemical switching. Application of an electrical potential to a material could result in an increased binding affinity of select polarizable gases, such as CO_2, over other gases present in the process stream (e.g., H_2O, N_2, O_2). Alternatively, application of an electrical potential could result in a conformation change in a material (e.g., alignment of surface functional groups), resulting in a change in gas binding affinity. For example, it has been shown that induced electrochemical potentials can enhance binding to certain gases in MOFs.[7] As shown in Figure 27, electrochemical reduction of an MOF produces an enhancement of H_2 uptake. An extension of this concept that generates a triggerable, reversible binding of CO_2 could serve as a smart capture agent. It should be noted that this proposed approach is distinct from a currently available technique, electric swing adsorption, which involves simple thermal heating of the adsorbent by resistive heating. Membranes have also been developed that use an electric potential gradient to create the separation driving force.

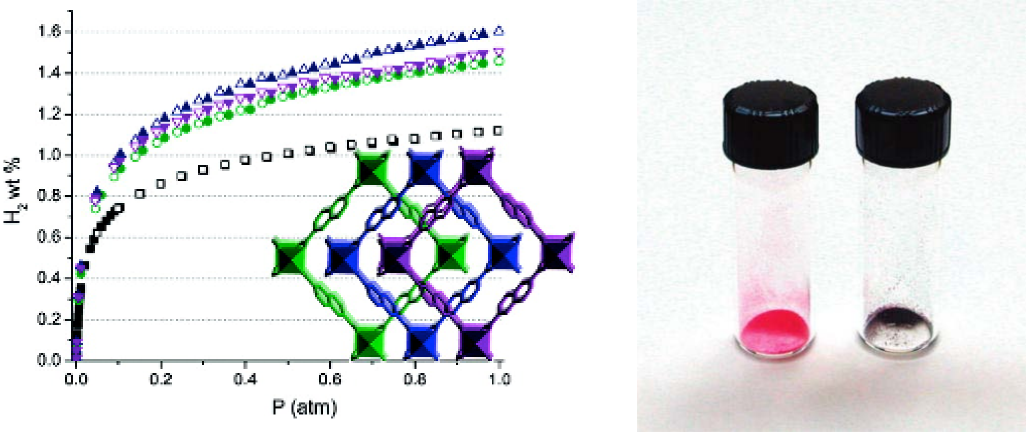


Figure 27. Chemical reduction of a porous material. Reduction and cationic doping of a porous MOF results in polarization of the surface and enhanced binding of gases (H_2) as shown in the colored isotherms (left, unaltered material shown as black squares). Reduction and doping is apparent by the color change (right, change from pink to dark purple) in the material.[7]

Electromechanical switching. The piezoelectric or electrostrictive behavior of certain materials has the potential to induce structural changes that would modulate gas binding affinity.[8] These structural changes could occur at the molecular level (e.g., site of CO_2 binding) or at the bulk level, resulting in a switch-like open–close reaction.

Electromagnetic irradiation and stimulation. Radiation at various wavelengths—microwave, radiowave, and perhaps even visible light (Figure 25)—has the potential to induce a change in gas binding or to change the size of a pore, thus serving as a trigger for capture/release. This change in binding could result from resonance phenomena associated with the material, the bound gas species, or both.

Magnetic switching. Magnetically switchable materials could be developed that display changes in binding affinity for a target based on changes in external magnetic fields, spin states, or other parameters. Magnetostrictive materials, which change structure upon application of a magnetic field, are another intriguing approach that may tune separation selectivity and efficiency.

Triggered phase transitions. Changes in the phase of a material could result in changes in gas binding affinity or capacity. Such alterations of phase could be modulated by secondary stimuli, including gas sorption (Figure 24) or other stimuli mechanisms described earlier. The capture of gases during a solid state phase transition in a porous material has been described.[9] In a barium sulfonate network solid (Ba_3L_2, L = 1,3,5-benzenetrisulphonate), a conversion from open- to closed-pore phases results in mechanical trapping of atmospheric gases. This conversion is reversible, and exposure to ambient moisture results in the release of the trapped gases (Figure 28). Such a system, if sufficiently stable and if made selective for CO_2 or O_2, for example, could offer an intriguing dynamic phase-change material for carbon capture technologies.

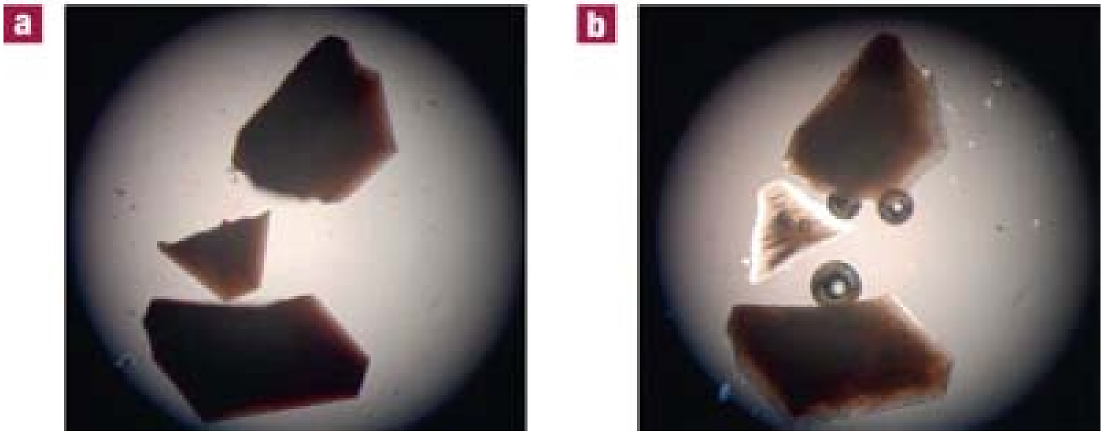


Figure 28. Mechanical capture of gases in a crystalline solid. A phase change in Ba_3L_2 (L = 1,3,5-benzenetrisulphonate) results in the release of atmospheric gases from the crystals, as evidenced by the formation of bubbles (right). In this case, the phase change is stimulated by a chemical signal in the form of ambient moisture.[9]

Many other potential stimuli could be employed with a new generation of materials for low-cost gas separations. For example, polymer membranes have been developed that control selective transport by response to triggers such as pH, ionic strength, temperature, light, magnetic field, and chemical stimuli.[10] Developing these separation schemes will require a new fundamental understanding of the chemical and physical processes that affect separation processes under alternative driving forces. This understanding will enable the development of an entirely new generation of smart separation materials with tailored architectures for responding to the driving force and assisting in the separation process.

Scientific Questions and Opportunities

Highly efficient and selective separation of small molecules or ions from complex mixtures is a critical need for both carbon capture and oxycombustion technologies. Novel approaches that use new materials and alternative driving forces have enormous potential for dramatically reducing energy costs that currently hinder separation technologies. These less expensive processes are critically needed to meet the daunting challenges required for carbon emissions mitigation in the future. However, the full potential of this vision cannot be achieved with incremental changes in currently available materials. These advances will be realized only with research focused on understanding the full array of chemical and physical processes that occur when a stimulus interacts with a materials system, so that the interactions can be tailored to optimize the capture and release of targeted gases.

Exploit nanostructure in separation efficiency. To develop new separation schemes based on alternative driving forces, revolutionary materials designed at the nanoscale to attain optimal separation efficiencies are needed. Nanoscale features have been shown to dramatically enhance flux and selectivity in polymer membrane separations and in solid sorbents. Tailoring nanoscale structure is a promising means of enabling low-energy pathways for selective capture and release driven by alternative forces.[10] Recent advances in the synthesis of polymers, inorganic materials, and organometallic materials with nanoscale structural features offer enormous potential for achieving optimized architectures that respond to external driving forces for efficient gas separation. Further, functionalizing the surface of these materials can provide another dimension of tuning to be used with a wide variety of potential external stimuli. To support the design and synthesis of these smart, nanostructured materials, advanced characterization and computational methods are needed for studying them under realistic conditions and elucidating and predicting mechanisms for gas separation. Understanding these molecular-level processes will underpin breakthroughs in the use of alternatives to pressure and vacuum to drive low-energy molecular and ionic separations.

Develop new separation functionality triggers. Forces for driving ion and molecule separations for carbon capture strategies could take any number of forms, including continuous or pulsed. Much of what we know today about alternative driving forces for separations is based on an Edisonian approach of trial and error. To expedite the discovery and deployment of membrane separation systems consisting of new materials and external triggers requires a fundamental understanding of the interaction of targeted molecules or ions with materials and the changes that occur when an external stimulus is applied. Developing this understanding will require advanced analytical tools to study the materials of interest under conditions that reflect the actual environment of the separation processes. In addition, new computational tools are needed to understand and predict the separation of targeted gas molecules or ions at the molecular level under the influence of the applied stimulus. Understanding the structure/performance relationships of these separations systems can drive the development of radically different separation schemes, including the possible application of a combination of driving forces in multifunctional separation materials.

Potential Impact

Current technologies used to reduce carbon emissions from combustion processes rely on highly expensive changes in temperature and/or pressure to cause gas capture and release, greatly impacting the ultimate cost of electricity in a power generation plant. The development of new smart materials with nanostructured architectures, possibly modified with specific functionalities designed to interact with innovative stimuli, has huge potential to increase separation efficiency and greatly reduce costs. Such novel processes could be game-changing, allowing effective use of carbon-based fuels without deleterious impacts on the environment. In addition, concepts developed as part of this research could have a huge impact on separation processes used across industry. Separation processes add huge energy costs to the production of biofuels, chemicals, pharmaceuticals, and other commodities; and new separation approaches could also make these processes more selective and more energy-efficient. Further, the new materials and processes developed as part of this research could impact a broad range of other applications in which smart, switchable materials are needed, including novel sensors, drug delivery systems, and others.

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CROSSCUTTING SCIENCE FOR ELECTRICAL ENERGY STORAGE

CROSSCUTTING SCIENCE FOR CARBON CAPTURE

CROSSCUTTING ANALYSIS TOOLS

Overview

The industrial revolution has been a catalyst for improving the lives of humans through the invention of many innovative technologies, from nylon to cell phones; but it is also the origin of the looming issue of climate change caused by carbon emissions. However, innovation can also provide revolutionary solutions to the carbon emissions problem through the development of novel materials and chemical processes that go far beyond today's technologies. A key to realizing new technologies to address carbon emissions is the development of new characterization and analysis techniques to meet science and engineering goals for carbon capture in 2020 and beyond.

During the course of the carbon capture workshop, several themes emerged that were centered on analysis tools required to develop revolutionary carbon capture technologies. First, state-of-the-art characterization tools that complement one another need to be integrated in such a way that the resulting data can be assembled to guide interpretation and modeling of experiments. Such multidimensional analytical information will revolutionize the way experiments are conducted and expedite the discovery of new materials and processes. Second, today's analytical tools fall far short of meeting the challenging needs for the study of carbon capture processes. New tools must be developed to address a range of specific challenges; examples of some of the crosscutting analytical information needed for several promising carbon capture technologies are provided below. Third, there is a critical, especially challenging need to develop analytical capabilities that can recognize unique events rather than measure ensemble responses as the currently available analytical tools do. It is the properties of these unique events that need to be understood and optimized. Finally, to produce the materials needed for efficient carbon capture, it is imperative that advanced characterization, advanced synthesis and processing, and advanced computation come together in a synergistic effort.

The Crosscutting Analysis panel identified analysis needs that support the priority research directions developed at the workshop. These analysis needs must be addressed to obtain critical pieces of information for characterizing, understanding, and ultimately improving upon some promising carbon capture technologies. These needs include

- in situ analysis across broad temporal and spatial scales
- examination of interfaces and thin films at the atomic and molecular levels
- an atomic-scale view of gas–host structures and kinetics
- understanding and control of nanoscale synthesis in multiple dimensions
- characterization for guided synthesis and processing strategies

Further details on these four key research areas are provided in this section.

In Situ Analysis across Broad Temporal and Spatial Scales

Processes for carbon capture typically operate under extreme conditions of elevated temperatures, pressure gradients, and high volumetric flow rates of complex gas or liquid mixtures; and they often occur in the presence of mechanical stress, impurities, and debris. The thermodynamics and kinetics of capture processes under these conditions are very different from typical laboratory environments. To develop fundamentally new processes, or even to improve the efficiency and reliability of existing processes, necessitates characterizing material behavior and chemical processes in situ under these extremely challenging conditions. Although there are techniques today that characterize materials in situ, they are quite limited in scope and in applicability to the study of carbon capture processes. It is critical to develop new analytical techniques that will allow researchers to examine the structure and properties of materials in situ **and** examine the dynamics of molecular interactions involved in both capture and release (regeneration) for a broad range of processes, including physisorption and chemisorption.

Accurate information on structural and dynamic properties in situ is critical to enable materials by design for breakthrough improvements in key transport, reaction, and thermodynamic properties under actual conditions of operation. New analysis tools are required for studying structural and dynamic properties of materials under a wide range of pressure, temperature, and other conditions. Such studies may include, for example, varying pressure–temperature conditions with the material in contact with fluids, in the presence of reactive or corrosive gases, and over many cycles (aging). This capability will also be critical as we explore the potential for separations under conditions other than pressure and temperature, as outlined throughout this report. The ability to study materials under realistic pressure, temperature, and other operational conditions will impact not only carbon capture but also other broad areas of energy research, including catalysis, fuel cell energy conversion, and energy-efficient materials synthesis. To realize this potential, characterization techniques must be developed that can be applied in situ over the relevant span of time and spatial scales.

The structural and dynamic properties of gas capture materials (including solid sorbents, membranes, and complex fluids) determine the key thermodynamic and kinetic properties necessary for proper performance. The gap between model systems and realistic conditions can be bridged by in situ experiments. Some advanced materials characterization methods are particularly suited to in situ experiments, for example, hard x-rays and neutron beams that can penetrate bulk materials. However, even for these relatively established techniques, new capabilities are necessary to bring them to bear on the carbon capture problem, including the development of new sources and instruments to achieve adequate spatial and temporal resolution. And in many cases there is a lack of adequate sample environments that accurately simulate actual capture conditions. Thus new concepts are needed to develop realistic environmental sample chambers for use with a broad range of characterization tools. It may even be possible to devise novel nanoscale probes (i.e., nano “Mars Rovers”) with self-contained measuring capabilities that could be fully immersed in the environment to provide the ultimate in in situ characterization.

Even with optimal in situ sample environments and appropriately matched probes, limitations in the temporal and spatial resolution of measurements must be overcome. The time scales of importance to carbon capture processes span over 15 orders of magnitude, from sub-picoseconds (10^{-12} seconds) associated with an absorption event up to the many seconds required for the diffusion of heat and mass through critical systems. Similarly, length scales of interest span orders of magnitude from the atomic scale needed to understand the binding of gas–host with positional precision and compare it with theory, to the millimeter range of porosity in solid adsorbents. Further, it will be particularly important to combine multiple techniques to study a process/material simultaneously, providing multiple dimensions of information under the same conditions on the same sample.

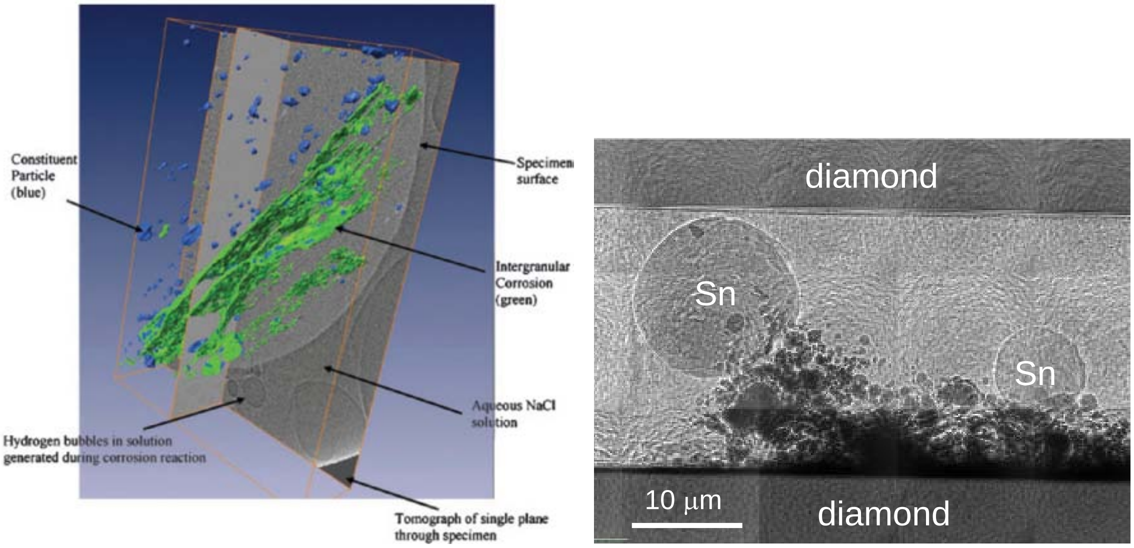
Dramatically improved performance from new analytical techniques is required to develop revolutionary carbon capture processes that meet the challenges beyond 2020. Outlined below are examples intended to provide inspiration for the development of new capabilities for developing new carbon capture materials and associated capture processes.

X-ray techniques. High intensity x-ray light source–based techniques can provide exquisite insight into atomic arrangements and oxidation states of materials. Hard x-rays (energies of 12 to 120 KeV or 0.10 to 0.01 nm wavelength) penetrate materials nondestructively. X-ray experiments can be conducted in experimental chambers to achieve high temperatures, pressures, and other environmental conditions required for studying carbon capture materials and processes. Less penetrating soft x-rays (energies of 0.12 to 12 KeV or 10 to 0.10 nm wavelength) can be used in conditions that approach realistic environments by introducing large pressure gradients over short distances with skimmers. Many techniques are already available for examining complex and amorphous materials, including x-ray diffraction (XRD), pair distribution function, x-ray absorption fine structure, and others. The source brightness sets the lower limit for spatial and temporal resolution, because it determines the maximum number of particles per unit of time that can be focused in a beam. Current synchrotron XRD measurements can be collected on millisecond timescales with fast detectors and in nanoseconds with streak cameras. Major improvements in x-ray source brightness, spatial and temporal resolution, and detection sensitivity are needed to advance carbon capture science. For example, new ultrafast free-electron lasers are being developed that will allow examination of single events on the femtosecond scale with atomic-level structural and chemical information. Conventional x-ray storage rings can be improved to produce high average brightness for time scales of 1 picosecond and above, and new x-ray sources that provide resolution at the nanometer range are on the near horizon. In addition, new techniques based on x-ray processes, such as imaging (see the sidebar "Viewing the Nanoscale with X rays"), have the potential to provide even more insight into gas capture and release processes that are needed to develop new carbon capture materials.

Neutron scattering. Neutron scattering, including diffraction (elastic) and inelastic measurements, offers important and unique capabilities to provide new understanding of molecular-level structure and transport in the complex, multicomponent environments encountered in gas separation processes used to reduce carbon emissions. The sample-penetrating power and light-element sensitivity of neutron scattering has been used to determine the crystallographic locations of absorbed gases in materials. The Fourier

Viewing the Nanoscale with X-rays

Development of x-ray nanoprobes at synchrotron sources has potential for providing unprecedented detail on interactions between gases, such as CO_2 and O_2, and potential hosts. For example, transmission x-ray microscopy (TXM) is a powerful tool for nondestructive in situ imaging with unprecedented spatial and temporal resolution. This is essentially the same concept used in medical x-rays and CT scanners, which provide doctors with in situ information on the internal “structure” of organs and bone in patients. Using high-resolution zone plate detectors, state-of-the-art instruments can currently provide spatial resolution in the 30–60 nm range. A single 2D radiograph based on x-ray absorption contrast can be collected in a few microseconds at bright synchrotron x-ray sources. When collected over many angles, these 2D images can be reconstructed into 3D x-ray tomographic representations, just like medical CT scans. As high-energy x-rays are highly penetrating, TXM could be adapted for in situ monitoring within complex, changing physical and chemical environments. However, substantial improvements in spatial resolution and imaging speed are required to address many of the challenges in carbon capture science to allow dynamic studies on the nanoscale. These will require coupled innovations in x-ray sources, optics, and detector instrumentation.



Left: Three-dimensional rendering of 200 synchrotron x-ray radiographs showing localized corrosion morphology within an aluminum specimen exposed in situ to a chloride environment. Rendering shows heat-affected zone near weld after 40 hours exposure to 0.6 M NaCl and highlights intergranular corrosion areas (green) and intermetallic particles (blue).[1] Right: Synchrotron x-ray microradiograph of tin spheres of varying size compressed between diamond anvils. The sample chamber is composed of beryllium, which allows transmission of x-rays and direct in situ viewing.

difference map method (Figure 29) can be used, for example, to probe the time-averaged CO_2 locations in solid absorbers such as metal-organic frameworks (MOFs) and zeolite inorganic frameworks (ZIFs). Further developments in sample environment pressure and temperature capabilities are needed to make possible such studies at the environmental conditions found in flue gases. These environments must also be adapted to the special needs of inelastic experiments, in order to understand diffusion rates and concentration profiles of gases in solid media. Additional challenges must be met to harness the power of neutron scattering to understand structure and dynamics in liquids and membranes. For liquids extractants,

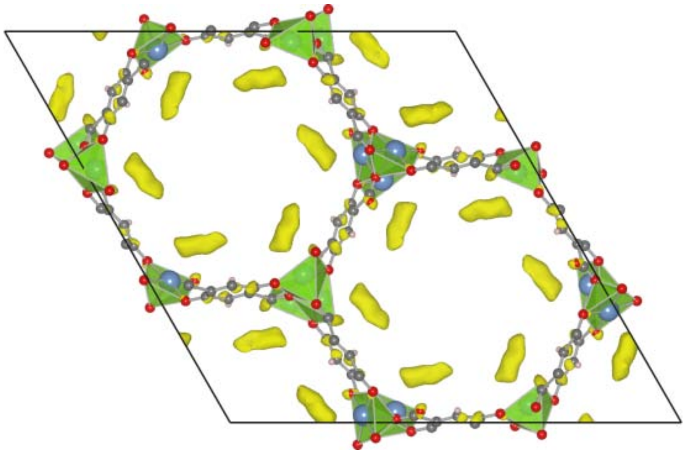


Figure 29. Neutron Fourier difference plot. The unit cell of the Mg–MOF$_{74}$ lattice is shown in green, red, and grey. CO$_2$ molecules are shown in yellow. It is obvious that the CO$_2$ absorbs in structurally specific positions in the lattice.

chemical stability in extreme environments is needed in addition to the demands of temperature and pressure. Scattering experiments to quantify the local structure (and hence solubility) of gases in liquids will push the limits of sensitivity and reproducibility in scattering experiments, made possible only through the availability of high-flux sources and optimized instruments. Similarly, the challenges of understanding structure and dynamics in thin-film membranes will push the limits of experimental capabilities in neutron reflectometry and grazing-incidence scattering. In addition, new optics and detector concepts are needed to push both the sensitivity and the spatial resolution of neutron-based techniques. Finally, the critical need for detailed information on transport and molecular environments in separation processes will be a key driver in advancing sample environments to access real materials under operating conditions.

Environmental electron microscopy. Recent developments in advanced electron optics and aberration correction have made it feasible to achieve sub-angstrom imaging resolution using transmission and scanning transmission electron microscopy (STEM). The coupling of these instrument innovations with novel designs for specialized in situ STEM holders (miniaturized flow-cells held within the microscope column) can allow for the direct imaging of materials behavior within a gaseous or liquid layer (e.g., in-cell environmental exposures) under heating, temperature cycling, potential cycling, mechanical manipulation, pressure, and other processes at high spatial and temporal resolution within the column of the electron microscope. Additional advances in in situ methodologies are needed to elucidate fundamental structure–property relationships, such as understanding the degradation of thin gas separation membranes under a variety of operating conditions relevant to carbon capture science. In addition, combining STEM techniques with other imaging, diffraction, and spectroscopic characterization techniques could provide multiple dimensions of information on capture materials and processes.

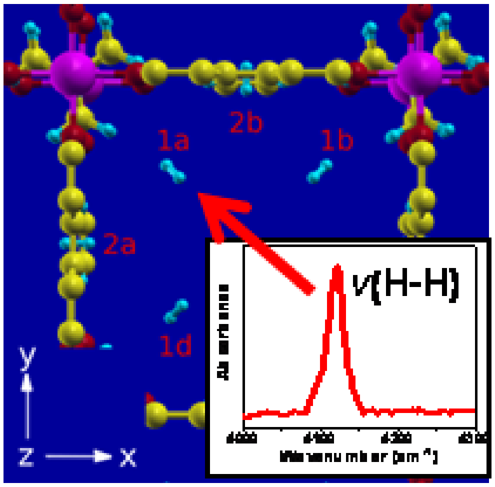
Scanning probe microscopy. Scanning probe microscopy (SPM) can provide high-resolution images of surfaces using a physical probe that scans the specimen. SPM has recently been adapted to examine the flow and absorption of mobile molecules and has the potential to uncover otherwise hidden details that govern the interaction between gases and various capture media. SPM allows very precise measurements of surfaces—changes in height of about 1 trillionth of a meter over regions as small as a few billionths of a meter. And, since absorption of a gas molecule will cause a material to swell slightly, SPM can detect local changes in volume, allowing the technique to “see” the movement of gas molecules, for example, into and out of a material. Because SPM may be operated under environmental conditions, measurements can be made as a function of pressure and temperature over a wide range of solid materials. Thus it may be possible to map exactly under what conditions and where a gas molecule penetrates a surface and how it moves around inside a solid. With this knowledge, it will be possible to understand the atomic-level details of gas interactions and transport. New modalities of SPM are needed to provide even more information on processes associated with carbon capture processes and to allow operation under a wider variety of environmental conditions. Combining SPM with other imaging and spectroscopic techniques offers great potential for multidimensional modalities of characterizing carbon capture processes.

Nuclear magnetic resonance. Solid-state nuclear magnetic resonance (NMR) provides a wealth of *structural* details from atomic-level to macroscopic length scales, and *dynamic* details from picoseconds to 10^3 second time scales.[2,3] Solid-state NMR methodologies most relevant to the characterization needs of solid capture materials, such as MOFs or ZIFs, can be found in studies of heterogeneous catalysis.[4] NMR exquisitely provides atomic-level details such as the structure, organization, and dynamics of gas binding sites, in addition to providing insights into kinetics, transport, and thermodynamic properties. NMR is particularly well suited for the study of adsorbents with the type of high-surface-area materials that will be used for gas capture processes used for reducing carbon effluents. Importantly, NMR is particularly powerful in obtaining structural and dynamical details in disordered materials for which conventional scattering approaches are ineffective. Magic-angle spinning (MAS) studies have even been successfully performed in situ in conditions typical for power plant postcombustion flue gas and precombustion water-gas shift reactors.[4] Further, in situ measurement of $^{13}CO_2$ adsorption in a variable-temperature MAS adsorption reactor, in combination with multiple quantum MAS and dipolar recoupling experiments to reveal the details of CO_2 bonding in a solid matrix, has the potential to provide a detailed understanding of CO_2 capture processes.

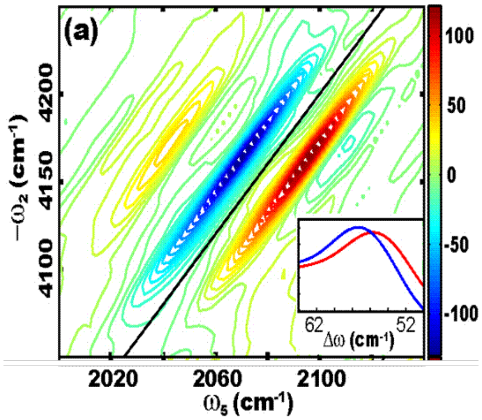
Optical and infrared spectroscopies. Optical and infrared (IR) spectroscopies have the advantages that they can be applied in situ, are highly sensitive, and can probe molecular and electronic structures to elucidate electrostatic forces involved in carbon capture, for instance. A number of spectroscopic techniques are already available to characterize vibrational or electronic molecular structure in realistic reaction environments. However, further improvements in the technologies are needed to catalyze the understanding and improvement of carbon capture processes. Nonlinear optical methods are especially needed, with bond-specific structural resolution and quantitative conformational information. Multidimensional IR and visible spectroscopies, such as 2D-IR and 2D-visible, that span time scales from the ultrafast to the ultraslow, are important tools for studying carbon capture (see the sidebar "Infrared Spectroscopy and Its Application to Nanoporous and Disordered Materials").[5] Cross peaks in these spectra will provide information on binding location and heterogeneity of the binding strength, stemming from vibrational and electronic couplings, which could then be studied over a large range of conditions and samples. Surface-sensitive sum-frequency spectroscopies (SFGs), especially heterodyned or multidimensional SFG, will aid in structurally specific binding studies and reveal differences in surface versus bulk adsorption. The development of novel spatially resolved nonlinear optical spectroscopies would also aid in the characterization of carbon capture materials. These techniques are

Infrared Spectroscopy and Its Application to Nanoporous and Disordered Materials

IR absorption spectroscopy is particularly useful for probing the interactions among guest molecules and nanoporous materials for storage and separation applications because it complements other physical measurements. IR absorption measurements are sensitive to the local geometry (adsorption sites) and to the details of the interaction potential.[6] Typically, the internal stretch of guest molecules (e.g., H_2, CO_2, CH_4) is shifted from its unperturbed position. For molecules with a center of symmetry (e.g., H_2), the mode also becomes IR-active because the interaction potential is not symmetrical. Information can be derived from IR absorption measurements with theoretical calculations. Quantum calculations deal well with weak interactions; however, they are expensive and slow for the large unit cells found in MOFs. A relatively new theory developed to treat weak interactions within a density functional theory framework, called van der Waals–density functional (vdW–DF),[7] appears to be able to treat large systems well. It should also be possible to apply nonlinear 2D IR spectroscopy to MOFs and other inorganic and/or disordered systems. 2D IR spectroscopy would improve the structural resolution by identifying the amount of symmetry breaking and resolve the inhomogeneous distribution of binding sites, for example.



Schematic of use of IR spectroscopy and vdW-DF theory to determine the possible adsorption sites for H_2 in an MOF material of the form M(bdc)(ted)$_{0.5}$ [where M=Zn, Ni, Cu; bdc=1,4-benzenedicarboxylate, ted=triethylenediamine]. The associated IR absorption spectrum of the H-H stretch vibration is superposed on the structure. Of the two possible distinct sites 1 and 2, only site 1 has a detectable dipole moment, although both sites exhibit similar H-H stretch frequency shifts (from the frequency of the unperturbed H_2 molecule). *Source*: N. Nijem, J. F. Veyan, L. Kong, K. Li, S. Pramanik, Y. Zhao, J. Li, D. Langreth, and Y. Chabal, “Interaction of molecular hydrogen with microporous metal organic framework materials at room temperature,” *J. Am. Chem. Soc.* **132**, 1654–1664 (2010).



A 2D-IR spectrum of the azide ion in an ionic glass. The elongated peaks indicate that the azide ion is extremely inhomogeneously broadened. That is, the 2D line shapes provide information on the distribution of vibrational frequencies, which are related to the disorder of the electrostatic environment around the azide ion. *Source*: E. C. Fulmer, F. Ding, P. Mukherjee, and M. T. Zanni, “Vibrational dynamics of ions in glass from fifth-order two-dimensional infrared spectroscopy,” *Phys. Rev. Lett.* **94**, 067402 (2005).

especially beneficial in that molecular dynamics simulations can be converted into IR spectra very accurately for a direct comparison between theory and experiment.

Examination of Interfaces and Thin Films at the Atomic and Molecular Levels

Interfaces—between gases and various solid and liquid separation media—play a critical role in approaches for isolating a targeted gas from a mixture. The structure and dynamics occurring at an interface determine important transport and reaction kinetics for gas capture and release. Near-surface properties govern wetting in ultrasmall capillaries, and the kinetics of exchange and reaction at these interfaces are difficult to examine nondestructively in bulk matter. It is particularly difficult to characterize the critical few atomic or molecular layers that effect separation at an interface in the presence of the much larger bulk materials. Advanced analytical tools are needed that are sensitive to determining the structures and processes occurring at interfaces in the complex systems encountered in gas isolation systems. Advances in these analytical capabilities will enable the design of complex multiphase gas capture materials—such as membranes, solids, and complex fluids—with interfaces that will enable breakthrough performance in high-transport kinetics combined with low-energy-penalty optimized gas separation cycles required to reduce CO_2 emissions. Improved interfacial characterization methods for complex materials will also impact the ability to elucidate and design improved interfaces that are critical to many other fields of energy science, including catalysis, corrosion, electrical energy storage, and fuel cell energy conversion.

Currently, there are a few tools that can examine interactions at well-ordered surfaces; but as these interfaces become more complex, the options become quite limited. New methods are needed to identify the near-interface composition and activity, and to profile this critical region as a function of distance from the surface. Techniques such as neutron and x-ray reflectivity provide profiles of solute concentrations over subnanometer distances near interfaces. X-ray photoemission using intense and angle-tunable sources can give elemental distributions over nanometers at interfaces. Light scattering techniques may also be used during the growth of thin membranes to relate the time-dependent measurements to position in the growing membrane. Nonlinear optical methods can selectively study dynamics and vibrational and electronic structure at solid–liquid and liquid–liquid interfaces. Other types of tools can be imagined—x-rays; electron and scanning probe microscopy; optical, magnetic resonance, and neutron scattering—that would exploit capabilities of both laboratory-based and user facility–based instruments. In addition, deeper understanding of interface-specific spectroscopies (e.g., nonlinear optical, photoemission) and existing surface-compatible spectroscopies (e.g., IR, Raman, x-ray photoelectron spectroscopy) is needed to apply these techniques to complex, poorly ordered interfaces.

New tools are also required to measure the mechanical, thermodynamic, and transport properties in ultrathin films (<100 nm). As outlined in the Membranes panel report, ultrathin membranes are highly desirable for isolating gases, such as CO_2 and O_2, from complex mixtures because of their high permeance; however, the challenge is that they must be mechanically, thermally and chemically robust. While this is challenging in its own right, even for a uniform membrane, highly functional solids and membranes of the future will likely be structured in three dimensions at the nanoscale. These nanostructures will require highly sensitive characterization techniques with unprecedented high spatial resolution.

A particular challenge is to combine structural and dynamic techniques with simultaneous measurement of mechanical and other properties. For example one approach to determining mechanical and transport properties is indirectly from interaction-potential sensitive techniques (IR, Raman, NMR), which are less invasive than, for example, direct mechanical measurements.

Measuring transport through innovative nanoscale geometries that are envisaged for tomorrow's membranes and adsorbents is a particular challenge for which no suitable technique exists today. Carbon capture science shares with all the basic energy sciences the need to develop revolutionary new tools for characterization of structure and properties down to the atomic level. The grand challenge is to know more and more about less and less material, avoiding as much as possible the ensemble averaging of the past.

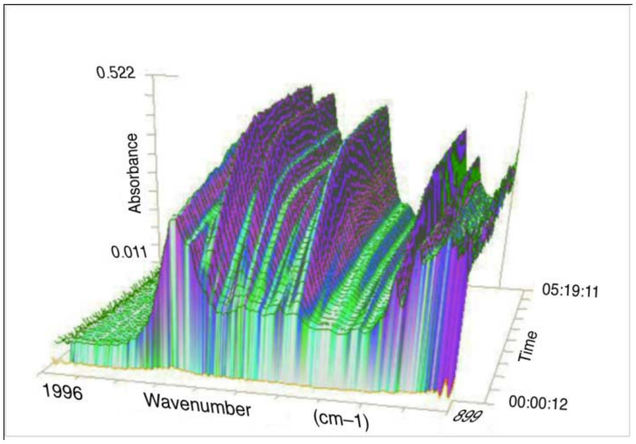
Achieving an Atomic-scale View of Gas–host Structures and Kinetics

To design better molecular "traps"—in adsorbant and absorbent systems—and more selective separation membranes, a greater atomic-level understanding is needed of gas–host interactions for adsorption sites and of kinetics (diffusion, reaction) and dynamics (vibrations, rotation, libration, translation) of molecules in complex media (liquids, solids) (see the sidebar "An Example of CO_2 Reaction Kinetics"). Experimental measurements of these critical phenomena are needed to validate and improve simulation and theory. Design of materials at the nanoscale offers the promise of tailored properties optimized for greater separation efficiency but will require guidance to reach desired configurations.

New characterization tools will provide key insights that will aid the design of a new generation of functional materials for gas adsorption and separation. The fruit of these studies is also critically important for advances in other energy technologies, including fuel cells, capacitors, batteries, catalysis, and high-surface-area materials. Specifically, there is a need to develop methods to deal with gas molecules in confined environments in order to study the molecular specificity and mechanism of gas loading, both CO_2 and O_2, in materials to develop new separation schemes for CO_2 reduction. These challenges become even greater when dealing with complex separation media, where both the location and dynamics of guest molecules in highly functionalized, 3D environments must be examined. Techniques such as elastic and inelastic neutron scattering and x-ray scattering, magnetic resonance, electron microscopies, and IR spectroscopy can yield this type of information; but they must be adapted to these systems. We aim to characterize gas organization, kinetics, and dynamics around adsorption sites in order to understand the chemical structure and molecular forces that aid in CO_2 and O_2 loading and ultimately in the design of improved separation materials. New characterization methods are needed to distinguish gas from host dynamics and distinguish, for example, bound CO_2 from gaseous CO_2. The grand challenge is to examine individual guest molecules, or at least ensure a full understanding of the nature of inhomogeneities in an ensemble. The grand challenge may be addressed by next-generation techniques with much higher sensitivity. Today individual guest molecules may be observed on surfaces in special cases by probe microscopy techniques. A major limitation of this approach is that the probe could be damaged by or interact with a loosely bound molecule.

An Example of CO_2 Reaction Kinetics Measured with IR Spectroscopy

The need for improved understanding of molecular-level interactions in capture systems can be seen in recent studies of the molecular mechanisms in the well-developed aqueous amine capture systems using monoethanolamine (MEA). While versions of this system have been used in industry for decades, its optimization with new capture materials requires further elucidation of the still poorly understood detailed reaction mechanisms. It is known that a key result of the process is the formation of an amine–CO_2 interaction called a carbamate, but only recently have time-resolved IR[1] and NMR[2] spectroscopy studies elucidated the actual detailed reaction mechanism necessary to form this species in solution on the capture side.



IR spectral surface between 2000 and 900 cm^{-1} for the reaction between aqueous 30.00 wt % MEA and a gas stream containing 13.04% CO_2. Several of the prominent growing peaks are identified as carbamate formed by amine-CO_2 interaction. In a CO_2 capture system, this carbamate is dissociated at higher temperature in a stripper column to release the captured CO_2. *Source*: P. Jackson, K. Robinson, G. Puxty, and M. Attalla, "In situ Fourier transform-infrared (FT-IR) analysis of carbon dioxide absorption and desorption in amine solutions," *Energy Procedia* 1, 985–994 (2009).

Thus new techniques with high temporal resolution are needed by which it may be possible to observe the molecule before disturbing it.

Beyond direct observation of guest molecules, there is often an associated disturbance in the host that is important to understand, since it plays a role in the energetics and dynamics of transport, capture, and release. The host disturbance can also reveal the position of the guest; it includes matrix structural deformation around the guest. At high gas loadings, effects should change and must be understood. In addition to matrix–guest interactions at high loading, guest–guest chemical interactions will grow and are important. Multidimensional IR and optical spectroscopies might be well suited to these tasks because they can measure electronic and/or vibrational coupling between host and guest to identify the binding site and associated structural changes. Well-established pulse field gradient NMR methods[8] can be exploited to measure gas diffusion in complex media. Changes in the host structure with gas adsorption can be monitored with conventional multinuclear MAS NMR.

In addition to understanding the static guest–host configuration, it is critically important to measure the kinetics and dynamics of these interactions. From IR measurements we can spatially map the local interaction potentials and thus the energy landscape associated with binding. Where hindered motion occurs, it is important to study and control it because it alters the energetics and thus the binding affinity. Information can validate theoretical models and lead to a more fundamental understanding of transport. The kinetics of transport are very difficult to measure currently, especially in the lower-dimensional systems envisaged for nanostructured high-performance systems.

Just as in the static case, cooperative effects (gas–gas, host–phonon) are important and must be understood. A grand challenge for existing techniques lies in the need to make these measurements very locally in solid or liquid disordered systems. At very high loadings, the strong gas–gas and gas–host interactions may lead to rapid changes in chemical or mechanical behavior. These interactions could be useful if controlled. For example, mechanical changes could be used as a means to release an adsorbed gas with a low energy penalty, but they may also be damaging, for example, causing materials cracking and failure.

Understanding and Control of Nanoscale Synthesis in Multiple Dimensions

New separation media will require the design and synthesis of tailored 1D, 2D, and 3D structures with external and internal surfaces optimized with respect to geometry and functionality. Methods to probe nanoscale structures, including imaging (electron and probe microscopy), diffraction (x-ray, electron, neutron), and spectroscopy (e.g., vibrational, optical, electron, neutron) will be needed to visualize the structures. Methods are needed to aid imaging of nanoscale and mesoscale 2D structures using “tags” that could illuminate chemical or other activity (e.g., quantum dots or nanoparticles).

One-dimensional structures, such as nanotubes or pipes, offer a route to tailored membranes. Methods are needed to functionalize the openings of 1D structures (e.g., channels), such as aligned carbon nanotubes (to make tailored membranes) or external surfaces of nanoporous channels in crystalline and amorphous materials. Characterization methods are needed that will allow the chemical functionalization to be characterized at spatially restricted areas, such as openings of channels.

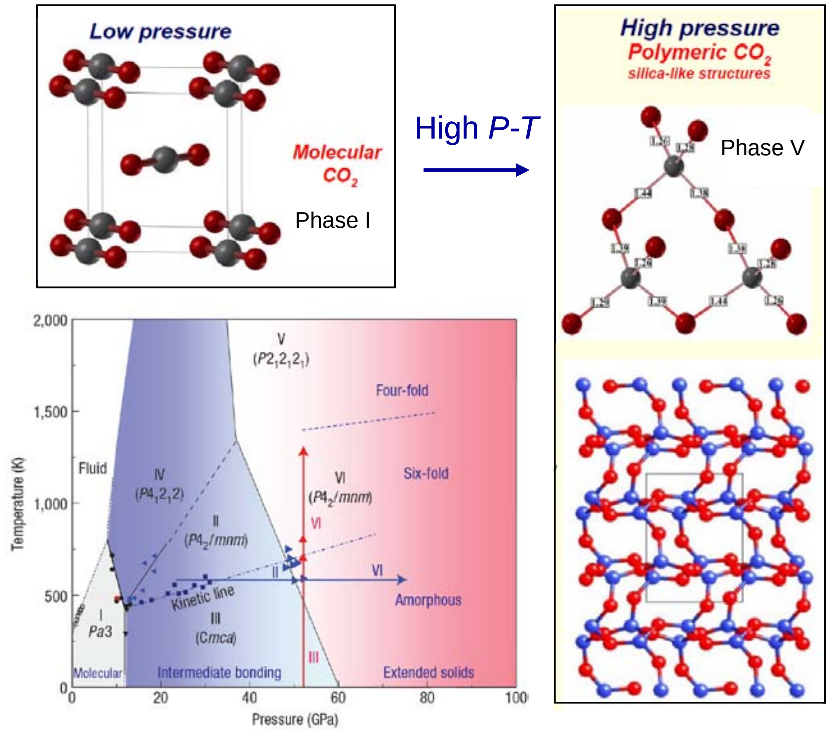
Characterization for Guided Synthesis and Processing Strategies

A very broad, important crosscutting theme emerged from the workshop that involves characterization and, equally, computation and materials synthesis. It is clear that all of the strategies for carbon capture are currently limited by the lack of high-performance materials. Current membranes, solids, liquids, and other critical components of an energy-efficient carbon capture system are not performing at the theoretical limits of what is possible. As a result, current carbon capture technologies are not energy- and resource-efficient; their inefficiency impacts their cost and application and causes them to fall far short of meeting needs for effective carbon capture strategies needed in the future. It became clear in the workshop that solving the technical bottlenecks in the development of new carbon capture strategies involves developing new materials and chemical processes with radically improved performance. The route to the required performance improvements was defined as a “design/control” or guided approach as opposed to a trial-and-error or empirical approach. To achieve this revolution in materials and chemical process performance will require very close coordination of novel materials synthesis and processing, state-of-the-art characterization techniques of the kind described in this section, and theory and computation.

Expertise and new capabilities in synthesis, characterization, and theory need to be fully coupled to meet the challenges of developing new carbon capture strategies. Characterization plays the ultimate role of validating the theory and simulation that will ultimately allow us to design the best possible material or chemical process based on required performance properties. But theory can also be used to shine the light on new materials and processes, guiding the synthesis of new materials (see the sidebar "Connecting Theory and Experiment." We are a long way from realizing this vision, and the concerted and integrated attack of the synthesis, characterization, and simulation triumvirate on carbon capture processes must be emphasized. The expected outcomes are tunable materials with localized dynamics ideally suited for capture, release, and transport control, and materials with hierarchical textures optimized for carbon capture, release, and separation.

Connecting Theory and Experiment: Polymeric CO_2 under Extreme Environments

When CO_2 is captured, it can form many different types of extended solids, depending on the pressure and temperature at which it is stored. Understanding and predicting which morphology it will adopt is important for knowing the energy cost and density at which it will be captured. The way to visualize these structures is by using a phase diagram, but it can be quite difficult to map an entire phase diagram. The one shown here was done using synchrotron XRD and Raman spectroscopy.[9] The phase diagram is also necessary for testing theory and computation to ensure that the predicted energetics are correctly modeled. Thus it provides guidance for designing novel materials.



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CROSSCUTTING COMPUTATION

The challenges posed by the need for innovative solutions to carbon capture cannot be met by experimentation alone. Cutting across all possible solutions—membranes, liquid solutions, solid sorbents, or other as yet unknown approaches—appropriate, innovative computation and modeling approaches are needed for significant progress in understanding routes to more effectively reducing CO_2 emissions. The capability to predict thermodynamic and chemical equilibria, reaction dynamics, and the transport of gaseous target molecules in liquid substrates or solid materials is essential for the design and optimization of carbon capture technologies. Even for established approaches, such as large-scale separation processes, such data are not always available. For example, although it is common to find measurements of pure component adsorption isotherms in the literature, isotherms for mixtures of gases are less often available for optimization and design. This lack of information often promotes the adoption of untested approximations of, say, the ideal behavior of the mixture in the absence of reliable data or predictions of mixture behavior. As methodologies for carbon capture advance, turning to new and different materials and conditions and different characteristic length and time scales, the relevant thermodynamic, transport, and kinetic data are even less likely to be available.

This situation creates a strong driving force to turn to computational calculations to predict properties that enable the design and optimization of new carbon capture processes. Computational approaches include first principles calculations (quantum chemistry, ab initio molecular dynamics), molecular simulations (such as molecular dynamics and Monte Carlo–based techniques), larger-scale computational routes (including coarse-grained simulations; solution of partial differential equations; and stochastic simulation-based approaches such as Brownian, dissipative particle, and Stokesian dynamics). A number of carbon capture mechanisms—for example, liquid absorption based on adsorbents that chemically react with CO_2 during CO_2 uptake (see the Liquid Absorbents panel report)—involve chemical reactions, many of which are ill-characterized or presently unknown. First principles methods can be used to determine reaction pathways and compute reaction rates. Molecular-scale simulations rely on the availability of accurate models for molecular interactions, known as force fields. While many force fields are available for small molecules such as CO_2, O_2, N_2, and water, cross interactions with the new materials that could be considered for carbon capture (e.g., carbon nanotubes, porous materials, polymers) may not be available. Parameterizing these interactions invariably requires first principles calculations (e.g., quantum chemistry calculations) and knowledge of the interaction between the guest molecule and host molecules. For ordered crystalline materials, the host structure is well understood; however, for many complex materials, including amorphous materials, these structures are poorly characterized and new means to create representative structures of amorphous materials are needed.

Once the required parameters are available, molecular simulations can readily be carried out to determine thermodynamic equilibria and transport of guest molecules at process conditions. Coarse-grained and other mesoscopic simulation techniques also have a significant role to play. Molecular simulations can take advantage of explicit representation of each atom in the system by simpler objects (e.g., beads or other geometric shapes) that retain the essential geometry and interactions of the particles. Such representations allow consideration of far larger system sizes and time evolutions, which can help bridge the gap between representations of atomic-level and macroscopic processes and hence allow a more facile comparison with experimental data (where such data exist). Unfortunately, the lack of ready access to parameters for coarse-grained simulations is even more acute than for molecular simulation and deserves more attention from the community. Similarly, deterministic and, increasingly, stochastic simulation approaches are needed to describe reaction-diffusion processes relevant to many carbon capture technologies at scales that facilitate comparison with experiments.

Up to this point, the traditional role of molecular simulation has largely been to provide insight into a mechanistic understanding of known materials and processes and offer the ability to optimize both. However, there is tremendous potential for it to play a more extensive and predictive role in the design of novel materials in advance of experimentation. Eventually it will be possible to predict macroscopic properties of materials accurately using representative atomic, molecular, and coarse-grained potential models and appropriate simulation techniques. Once this capability exists, through the process of reverse-engineering or "inverse design," simulation can provide candidate materials that satisfy desired properties or characteristics. Some such techniques, such as reverse Monte Carlo and genetic search algorithms, are already available, but more innovative search techniques are needed. Inverse design (see the sidebar "Inverse Design of Capture Molecules") constitutes a "grand challenge" for molecular simulation. It has enormous potential to benefit the carbon capture community, particularly in discovering materials that might not be found by the more traditional routes of searching known classes of materials with suitable properties.

There are thus three sets of challenges and opportunities for advancing carbon capture capabilities using theoretical, computational and modeling tools:

- Creation of a *molecular toolbox* of simulation methods and models to describe guest (gas solute) and host interactions and the host structure of complex noncrystalline materials
- The prediction of *thermodynamics and transport properties*, especially absorption, adsorption, diffusion and rate kinetics (for systems involving reaction)
- *De novo search and discovery* of novel materials

Underlying and facilitating all of these tools are first principles calculations, as methods to calibrate force fields, to characterize reaction pathways and reaction kinetics, and to predict structures of interfaces.

SECTION I: EXPANDING THE MOLECULAR TOOLBOX FOR GUEST-HOST INTERACTIONS AND HOST STRUCTURE MATERIALS

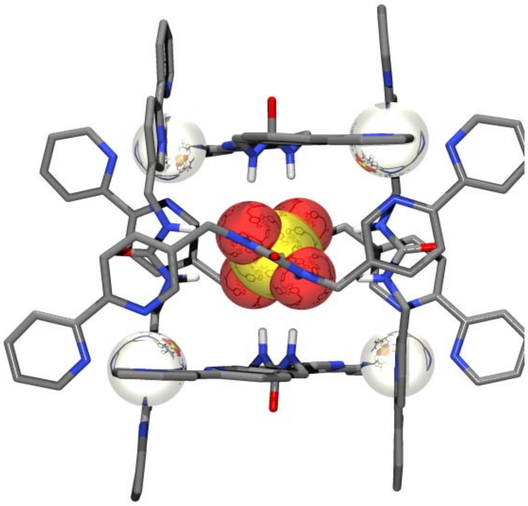
CURRENT STATUS

The range of potential models and simulation techniques, a virtual "molecular toolbox," is critically needed to simulate the broad range of dissimilar molecular interactions and complex material structures found in future carbon materials. While there have been great strides in the advancement of computational tools and methods over the past couple of decades, further advances in molecular models and techniques will be crucial to accelerate the discovery of carbon capture materials that efficiently separate CO_2 at the levels necessary beyond 2020.

Inverse Design of Capture Molecules

Protein receptors and enzymes are valued for their abilities to effectively bind substrates, stabilize reactive intermediates or high-energy conformations, and catalyze chemical transformations. Chemists have attempted to develop molecules with these same attributes, but the identification of host structures capable of recognizing a specific guest remains a grand challenge. This challenge can be addressed with a computer-aided design approach in which molecular fragments are assembled to generate candidate structures and a variety of computational models are used to rank them. The ability to design chemical structures with predetermined functionality is the key to finding new materials for energy and other new technologies. A particular challenge is developing separation agents for the selective removal of components in complex mixtures, such as those found in carbon capture schemes.

The power of using a computational approach to guide experiment was recently demonstrated in the design of a self-assembled cage that binds sulfate with remarkable affinity (right). It is notoriously difficult to remove hydrophilic anions like sulfate from aqueous solutions. Molecular modeling showed that six urea molecules could hydrogen-bond to sulfate, yielding a complex with tetrahedral symmetry. It was reasoned that a self-assembled cage could adopt this arrangement if each urea molecule were the edge of a tetrahedron held together by nickel tris-bipyridine vertices. Starting with this as a basis for the design, the challenge was to identify linkages between the urea and bipyridine groups to generate molecular components that would favor the desired arrangement. This was done using computer-aided molecular design methods in which more than a quarter million possible linkages were evaluated within minutes. After further evaluation with molecular dynamics calculations, a small list of promising candidates was generated. One of these "designer" cage components was synthesized and, when mixed with nickel sulfate, yielded the predicted tetrahedral cage. This result represents the first time that guest binding within the cavity of a self-assembled cage was predetermined. The precise positioning of the binding sites within the cage resulted in a very strong receptor for aqueous sulfate, on a par with sulfate-binding protein.



Source: R. Custelcean, J. Bosano, P. V. Bonnesen, V. Kertesz, and B. P. Hay, "Computer-aided design of a sulfate-encapsulating receptor," *Angew. Chem. Int. Ed.* **48**, 4025–4029 (2009).

Complex Molecular Interactions

The availability of accurate force fields that define intermolecular interactions is key to the success of molecular simulation in predicting the thermodynamic and transport properties of materials. However, accurate force fields are sometimes not readily available for materials of interest and for mixtures, even for relatively simple gases from a molecular standpoint. Progress requires a better understanding of the interactions of key targeted gas species or “guests” (e.g., CO_2, CH_4, N_2, O_2, H_2O) with complex materials such as ionic liquids, polymers, metal-organic frameworks (MOFs), carbon nanotubes, and other as yet untried materials. To predict adsorption isotherms, it is insufficient to characterize only the local interactions with, for example, one well-defined metal site or ionic molecule. The primary current method of obtaining force field parameters for advanced carbon capture material is to use standard literature force fields for CO_2, and other available force fields for materials such as zeolites, polymers, or ionic liquids. There has been some use of a combination of first principles calculations and literature force fields in the framework of molecular simulations; clearly, automated methods of developing force fields systematically from first principles methods are needed. For the reactive force field ReaxFF—used in classical molecular dynamics simulations that allow for the the possibility of chemical reaction—methods have been developed for automated force field fitting to first principles calculations.[1,2] Other methods include matching some force field parameters to experimental isotherm data, although experimental data are too limited for this to be the standard method for obtaining force field parameters.

For example, if we consider the adsorption of CO_2 within an MOF, selectivity for CO_2 is determined not only by the interaction with the exposed metal site but also by the topology of the framework. This environment requires knowledge of accurate charge distributions and dispersive interactions beyond the accuracy currently available. This problem is commonly addressed empirically by selective inclusion of experimental data. Examples exist where the availability of isotherms from existing data can be relied on to fit to parameters in the models, but these are scarce. The use of experimental data is further complicated by the fact that these isotherms invariably are not measured at conditions actually used in separation processes. Moreover, the isotherms are typically determined for pure substances; isotherms for mixtures are essentially unknown for systems relevant to carbon capture. Similarly, for polymers, ionic liquids, and other novel carbon capture materials, it is important not only to accurately characterize the local molecule-molecule interactions but also to characterize them in the context of the environment, including charge distributions and dispersive interactions. Truly predictive models, ones that do not require fitting force field parameters to experimental data, are needed to allow for the screening of potential CO_2 absorbing and adsorbing materials.

Complex Material Structures

In addition to improved characterization and prediction of intermolecular interactions between guest gas molecules and the host lattice of a crystalline material, a better, molecular-level, understanding of the structure of carbon capture materials is needed. Solid materials with rigid structures can be simulated relatively easily. However, for materials with amorphous or flexible molecular structures, finding even a suitable initial configuration that relates to the real material is much more challenging. The structure of materials with a high degree of ordering can be characterized quite readily through scattering techniques and the structures transferred to molecular models. The situation is less straightforward for polymeric systems, which are typically highly heterogeneous (Figure 30). Differences in process conditions may contribute to macromolecular structure differences and inhomogeneities in the polymer. The driving forces leading to these heterogeneous structures are not currently well known. The nonequilibrium state of glassy polymers often cannot be predicted because it depends on the processing conditions used to create the material. The situation is further complicated by the need to represent dominating physical and chemical characteristics, such as diffusion, porosity, tortuosity, and density of the polymer or polymer blend.

An area of new development in the field of carbon capture materials is the potential use of composite and mixed-matrix materials. These composite materials may include a large number of potential material and chemical combinations such as carbon nanotubes, composite polymer nanoparticles, and copolymers. These composite materials can exhibit complex structures (Figure 31) and chemistry. Developing a rational approach for selecting composites or mixed-matrix materials and optimizing their performance would provide a way to narrow down the immense number of potential combinations of materials that could, in principle, be incorporated into the composites and select a smaller set of candidates with the most promising properties.

Figure 30. Snapshot from a coarse-grained simulation of an entangled DNA polymer system featuring flexible polymers in a computer-generated periodic box. The "test" molecule (orange) is undergoing close frictional interactions (entanglements) with the shaded molecules; thus the test chain is undergoing reptation or snake-like motion. The lighter chains are free of the test chain. *Source*: A. Dambal, A. Kushwaha, and E. S. G. Shaqfeh, "Slip-link simulations of entangled, finitely extensible, wormlike chains in shear flow," *Macromolecules* **42**(18), 7168 (2009).

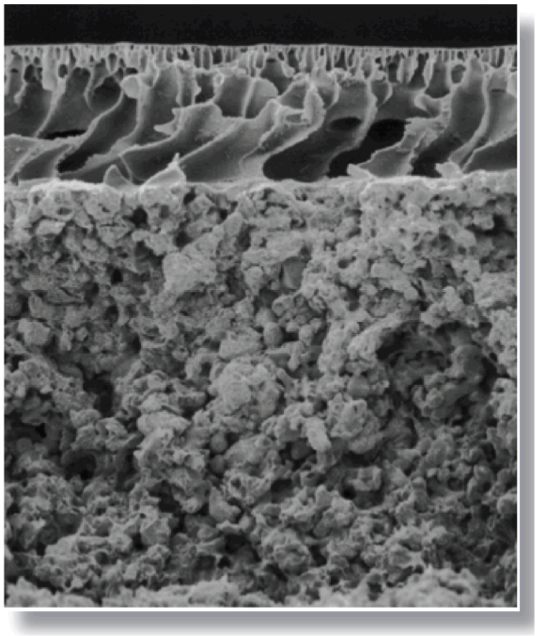


Figure 31. Scanning electron microscopy image of a poly-benzimidazole-based polymeric-metallic composite membrane cross section. The polymeric selective layer is the thin skin at the surface of the composite structure. *Source*: National Energy Technology Laboratory, "Thermally Optimized Membranes for Separation and Capture of Carbon Dioxide," Project Fact Sheet, 2008, http://www.netl.doe.gov/publications/factsheets/project/Proj194.pdf.

BASIC SCIENCE CHALLENGES AND OPPORTUNITIES

Along with its many challenges, this crosscutting PRD presents many opportunities. The opportunities and challenges are fundamental in nature, with the ability to inform and influence the design of materials at the macroscale.

Complex Molecular Interactions

The development of classical force fields informed by quantum calculations and experiment is one of the most fundamental prerequisites for scaling up the use of molecular simulation to design materials for carbon capture. Every atomistic, molecular, and coarse-grained model has force fields at its heart. As the need increases to scale simulations to longer time scales and to larger systems, computationally efficient but accurate force field functions and parameters will be needed. Researchers are currently limited by the tradeoff between accuracy and scale, each resulting in increased computational expense. To facilitate the development of novel carbon capture materials, these force fields are needed to enable the prediction of absorption isotherms for separated gases and gas mixtures.

One current challenge in the development and use of classical force fields is the lack of quantitative prediction of dispersive interactions and charge distributions for candidate capture materials. Ionic liquids, MOFs, and zeolites all contain unique charge distributions due to the presence of electronegative or electropositive moieties. These charge distributions are central to the unique absorption properties and must be accurately characterized in order to facilitate molecular simulations with predictive capabilities. Force fields for polymers also have limited accuracy when they contain rigid, associating, or polar moieties (Theodorou 2006a).

Beyond the Coulombic and dispersive interactions that can be represented using classical force fields, there is a research opportunity that includes the use of appropriate first principles calculations in situations where this level of theory is essential, including situations involving reactive interactions. These reactive systems, which include effects of electron transfer beyond polarization, will result in the formation and destruction of covalent bonds. Thus they must be calculated using first principles methods, which typically scale as $O(N^3) - O(N^7)$, where N is the number of nuclei, compared with molecular dynamics methods that scale as $O(N^\alpha)$, where $\alpha \cong 1$ for systems with short-range forces and is much less than 2, even for systems with long-ranged (Coulombic) forces. Clearly, first principles methods are used only in those situations in which the additional accuracy is critical and computational cost is justified. Advances are particularly necessary in quantum mechanically–based approaches (i.e., improving the scaling behavior of first principles methods) or hybrid approaches that can represent liquid phases and are computationally tractable,. In addition to hybrid schemes, in which a region of the simulation (e.g., around a potentially reactive site) is performed at the first principles level, while the remainder of the simulation is treated classically, another approach is the use of reactive force fields. Reactive force fields approximate first-principles modeling of chemical reactions by including calculated-on-the-fly bond order parameters (i.e., the effective charge and bonding state of each atom, which is clearly different for a carbon atom, for example in CO_2 versus CH_4, versus a bicarbonate ion).

Complex Material Structures

For a crystalline material, the major disruptions to the repeating crystal pattern are found at grain boundaries or defects, and these are often well characterized. In contrast, for amorphous materials with no discernable, long-range order, even the concept of defects is unclear; and few if any “gold standard” structures of representative amorphous materials exist. For materials with complex structures—particularly amorphous, composite, mixed-matrix, or even nanostructured fluids—the ability to construct molecular configurations as a starting point for a molecular simulation representative of the real material is itself a tremendous challenge. However, there are significant opportunities to integrate experimental and computational methods to build representative models of noncrystalline materials. By characterizing the complex material structure through x-ray and neutron scattering or nanoscale spectroscopic techniques (as outlined in “Crosscutting Analysis Tools”) and coupling this structural information to the molecular models, it may be possible to build realistic descriptions of some of these complex materials.

The combination of representative nanoscale materials structure for complex materials with accurate molecular interactions will significantly enable the prediction of structural property changes due to process changes, including instances when perturbations to the material structure are prompted by the presence of CO_2 or other guests. The broader challenge will be to develop predictive capabilities for increasingly complex materials, for which gold-standard structures for amorphous (or other complex) materials may well be essential.

An additional complication of many real materials used in carbon capture is that processing conditions can have large effects on the overall properties of self-organized material, yet the use of simulation to capture materials processing is nascent. This situation provides an incentive to develop novel carbon capture materials through *in silico* modeling of the effects of *processing* techniques and *processing* conditions on nanostructures or microstructures of these materials. If successful, this approach would significantly reduce the cost involved in developing and optimizing new separation processes, which currently rely on trial-and-error, incremental improvements.

Materials with such complex structures will become increasingly more difficult to simulate using atomistic methods, and it will be essential to link atomic-structured or nano-structured descriptions to multiscale models that can represent links to macroscale and experimentally accessible data. This would certainly improve the performance of membrane approaches to carbon capture, which typically involve composites or mixed matrices and may involve more exotic materials in the future. Developing a rational approach for selecting a material and optimizing its performance is ultimately an opportunity for computational methods to assist in the design of novel materials for carbon capture.

SECTION II: THERMODYNAMIC AND TRANSPORT PROPERTIES: ABSORPTION/ADSORPTION AND DIFFUSION

The successful development of a variety of technologies for carbon capture is crucially dependent on achieving the desired *selectivities* for separating gaseous mixtures of CO_2/N_2, CO_2/H_2, CO_2/CH_4, and O_2/N_2, among others. Addition of other species, such as H_2O and SO_2, often introduces further complications. The separation selectivities are dictated by a combination of two factors: (1) absorption or adsorption selectivity and (2) diffusion selectivity. For optimum separation both these factors need to complement each other.

CURRENT STATUS

Sorption selectivity depends on the thermodynamic equilibrium between the bulk gas phase mixture and the liquid, polymeric, or crystalline solid material, whereas diffusion selectivity is dictated by the rates of transport of guest molecules within the host material. Both sorption and diffusion selectivities are dependent on a variety of factors such as the distribution of active sites, framework charges, presence of cations, pore size, pore topology, and connectivity. For ordered crystalline microporous materials such as zeolites (crystalline aluminosilicates), carbon nanotubes (CNTs), and MOFs, there is a wide variety of channel sizes, topologies, and connectivities, as illustrated in Figure 32. Reliable estimations of phase equilibria, in combination with mixture diffusion, are an essential requirement for process development and design. In practice, such estimations are not possible purely on the basis of experiments because mixture isotherms and diffusivities are more difficult to access experimentally. Use of molecular simulation techniques such as Monte Carlo, simulations in the grand-canonical ensemble, molecular dynamics, kinetic Monte Carlo, and transition state theory offer potent alternatives. However, the data accruing from such simulations need coarse-graining to obtain parameters required for use in more commonly used continuum models for describing mixture adsorption and diffusion, such as the ideal adsorbed solution theory and the Maxwell-Stefan diffusion formulation. At present, only for ordered perfect crystalline materials with rigid structures, such as zeolites and MOFs, can these thermodynamic and transport properties be predicted with a reasonable degree of confidence.

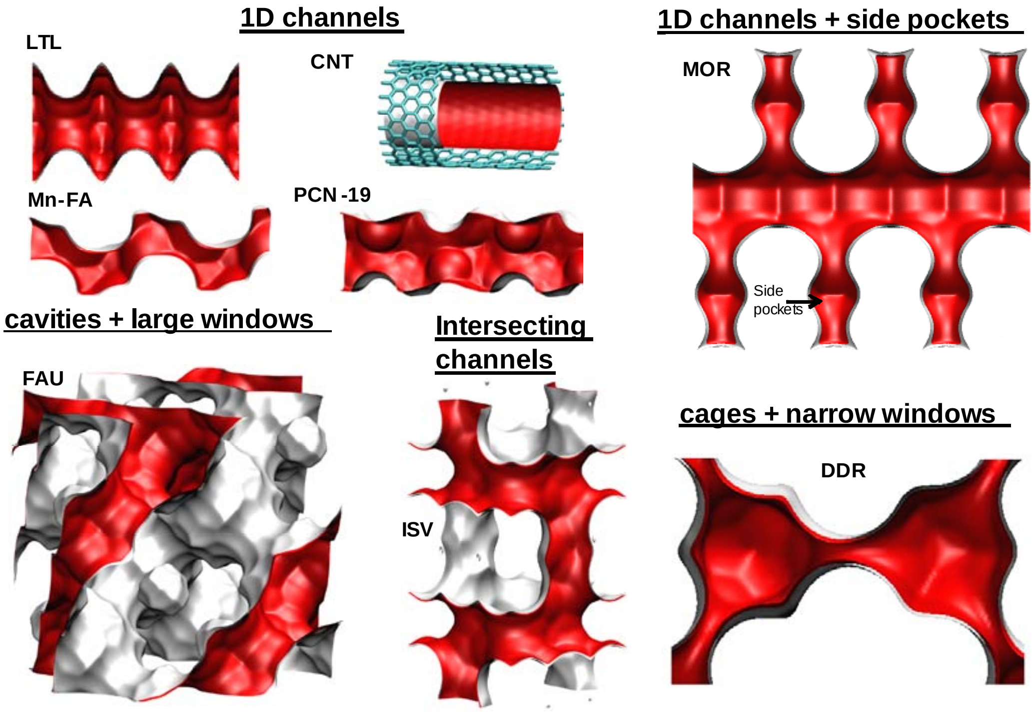


Figure 32. Examples of the variety of channel topologies and connectivities in zeolites, metal oxide frameworks, and carbon nanotubes. *Source*: Reprinted with permission from R. Krishna, "Describing the diffusion of guest molecules inside porous structures," *J. Phys. Chem. C* **113**, 19756–19781 (2009). Copyright 2009 American Chemical Society, where abbreviations for structures in this figure are referenced.

BASIC SCIENCE CHALLENGES AND OPPORTUNITIES

When accurate force fields are available, together with detailed atomic structural information, it is possible to obtain simulation data on the required mixture isotherms and diffusivities inside the “bulk” material. However, just understanding these bulk systems is insufficient for understanding the behaviors of materials as used in separations. For example, in actual applications these bulk materials need to be integrated in a separation device. The presence of any such device will create a gas/material interface, which can be an additional barrier for the transport. Recent work has shown that the surfaces of crystalline materials have different transport properties from the crystal interiors. Such surface resistances influence separation selectivities, and there is a need to develop the proper simulation tools for their determination. Modeling of the interfaces between gases and ionic liquids also needs similar attention and analysis.

In addition, one needs an understanding of the role of defects, impurities, and other surface characteristics that cause deviations from the bulk properties of the materials. As these effects exceed, by many orders of magnitude, the longest time and length scales that can be simulated with conventional algorithms, reliable coarse-grained models must be developed that can incorporate these effects and make the link between the atomic scale of a material and the continuum scale used in process design. Such a strategy typically consists of several interconnected levels, each level addressing phenomena over a specific window of length and time scales, receiving input from finer-grained levels and providing input to coarser-grained ones.[3] These models should be able to provide a better link between molecular diffusion and macroscopic transport through materials.

Observations that targeted gas molecules change the properties of the materials are also a particular interest. For example, CO_2 and H_2O have been found to induce structural changes in the host crystalline structure, and similar observations have been made for adsorption-induced swelling of polymer materials. The development of appropriate simulation methods that take structural changes into account is an important challenge, which requires an accurate description of phase changes of the host material. Ultimately, a better understanding of these effects should result in separation concepts that take advantage of the phase changes to reduce the energy costs of an adsorption/desorption cycle in a separation process

SECTION III: *IN SILICO* SEARCH AND DISCOVERY OF NOVEL MATERIALS

CURRENT STATUS

Most current research activities involving theory, modeling, and simulation of chemical systems related to carbon capture are aimed at predicting properties of experimental systems. This approach focuses on synthesis of materials and structures that are easy to synthesize or closely related to other known materials. Clearly, there is considerable unexplored opportunity to look for structures beyond these constraints that may provide unexpected and more optimal solutions for carbon capture applications.

The grand opportunity offered by computational techniques is to transform the portfolio of possible applications to include prediction or design of new chemical systems *de novo*. Such *in silico*-designed materials could be the result of either rational design or systematic search and could offer more nearly optimal properties for a given application or process. Carbon capture research could also greatly benefit from a “reverse engineering” approach through unorthodox or novel applications of existing or new computational tools, which could be used to discover materials that closely match a desired set of properties. Computation-based discovery has the potential advantage of being able to find optimal materials among known classes (e.g., the best amine for liquid capture, or the best MOF for solid adsorption). This approach could also discover novel materials not related to any currently known chemical systems.

BASIC SCIENCE CHALLENGES AND OPPORTUNITIES

The problem of identifying the best molecule or material for a given application is common across areas of chemistry. The most advanced approaches to molecular discovery are in use in the drug discovery field, where they are known as “cheminformatics.” Cheminformatics is focused on storing and processing data representing large sets of chemical structures. Given the success and wide implementation of cheminformatics techniques in the pharmaceutical industry, it is intriguing to ask whether similar approaches could be developed to discover unimagined systems of materials and/or processing techniques particularly suitable for carbon capture.

Two different approaches for the *in silico* discovery of new materials can be envisioned: virtual screening and inverse design. Virtual screening starts with a database of possible structures, which are then prioritized according to an assumed/estimated measure of the extent to which they meet set points of desired properties. Inverse design, in contrast, requires knowledge of some or all of the relationships between properties and structure. This knowledge base is then used to directly predict structures with a given (desired) property.

Discovery by Screening

The critical part of discovery by virtual screening is the availability of structural databases. For example, commercially available databases (or databases of commercially available compounds) can be screened to identify new amines to scrub CO_2. Extending these databases to materials that have not yet been synthesized would allow us to explore the limits of maximum achievable performance. In drug design, generation of virtual libraries of drug candidates is relatively straightforward, as it requires merging organic fragments to produce relatively small molecules. Similar search strategies for inorganic materials, in contrast, lead to a combinatorial explosion of a number of structures that would have little chemical relevance. Developing design strategies for databases of hypothetical materials that have a reasonable chance of being synthesized remains a key challenge.[4] The generation of a database of hypothetical materials is the first step to discovery of novel materials. Another anticipated challenge involves the screening of such databases to identify structures with closer to optimal performance. Given the very large number of pore structures, these screening strategies must rely on algorithms that can characterize the pore topologies (Figure 33). Molecular simulation techniques are too time consuming to screen the many million structures and screening strategies needed to find the optimal material.

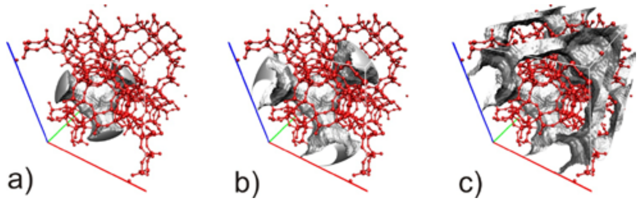


Figure 33. Partial differential equations (PDE)-based techniques can be used to automatically analyze 3D structures of porous materials. These images show how a PDE-based front propagation method is used to map accessible void space inside porous material. *Source:* M. Haranczyk and J. A. Sethian, *Proc. Natl. Acad. Sci.* **106**, 21472 (2009). Reprinted with permission.

Discovery by Inverse Design

The concept of inverse design represents an exciting and largely unexplored opportunity to identify optimal materials for carbon capture applications and many other design targets. Given a known property–structure relationship, one could envision algorithms that generate novel materials or molecules that directly satisfy the constraint of producing a desired property. For example, if the desired property requires, say, a nanoporous material with a well-defined pore topology, the inverse design algorithms would generate chemically accessible structures that have exactly the desired property. (See the sidebar "Inverse Design of Capture Molecules.")

Guided Synthesis

The preceding two subsections presented two approaches to facilitating the discovery of novel materials. These virtual materials would, however, need to be capable of synthesis before their performance could be verified experimentally. Thus the design of a realistic synthesis pathway for such hypothetical, search-generated, materials will present another considerable challenge for computational techniques. The synthesis of 3D solid-state materials requires a much better understanding of guided nucleation processes (e.g., how structure-directing agents or templates affect the nucleation barriers to create a variety of solid-state forms of matter). Additionally, more study is needed to understand how solution or processing conditions (solvents, aging, and environmental factors) and composition affect the self-assembly processes. Finally, computational elucidation of the principles behind hierarchical assembly is still a significant challenge. It is insufficient simply to know how to create/synthesize a desired molecular structure; competing thermodynamic and kinetic pathways that create undesired or unexpected structures must be inhibited or avoided.

IMPACT AND CONCLUSIONS

The crosscutting research directions discussed will have a large impact in facilitating and expanding the usefulness of computer simulation techniques (from ab initio to continuum-based approaches) to predict solutions for carbon capture scenarios. The provision of accurate transferable force fields and materials structures forms the bedrock of subsequent studies of specific candidate materials and processes for carbon capture. Better descriptions of these complex host materials and gas–host interactions will be essential for calculating phase equilibria, isotherms, estimates of permeability and selectivity for a specific solute (CO_2 or O_2, say), and the nature of fluid–fluid and fluid–solid interfaces.

Molecular simulation might be used to derive theoretical "upper bounds" for the anticipated separation selectivity for a given class of materials (e.g., ionic liquids, crystalline solids, polymers). Such an upper bound can help experimentalists in setting targets for materials development. For any given separation task, can molecular simulations help us decide a priori which class of materials is likely to be more effective?

New algorithm development and the development of the area of "inverse design" will play a key role in the expansion of computer simulation and modeling for carbon capture processes. The development of improved simulation techniques and coarse-grained models to handle mixture adsorption and diffusion inside complex materials will have a significant influence on the way we model adsorption and diffusion in diverse areas in the chemical process industries. These models are of special value in process optimization studies to determine the right set of process conditions needed to achieve maximum separation selectivities. Accurate models for adsorption and diffusion will also aid process development by cutting down the time required for commercialization. Broad searches through chemical space for novel materials offer the enticement of suggesting candidate systems with desirable properties and/or optimal operating conditions.

An exciting example of such a new technology might be designated as "a zero cost [carbon] capture toolkit," which would facilitate the discovery of materials for carbon capture. For example, electric power plants have low-grade energy that contributes little, if any, to the overall efficiency of producing electricity. Can materials be developed that use this heat for the carbon-capture process? Can a material be developed to release the captured CO_2 by an unconventional switching mechanism, such as light or pH changes, as opposed to traditional separations that release captured materials by a pressure or temperature swing? A suitably constructed search might identify novel and perhaps optimized materials processing routes using novel swing techniques.

But all of these advances will also have extensive corollary benefits, in application areas well beyond carbon capture, from providing better descriptions of polymers and amorphous or porous materials for semiconductor applications, including photovoltaics, to studies of geothermal energy, in which many of the same gas solutes encased in rock structures share the same modeling challenges. The availability of thermodynamic and transport properties could be of immediate benefit to process designers. Thus the general availability of reliable force fields and structural representations of complex materials will be an enormous asset to the scientific community in general. Studies of thermodynamic and transport properties for these complex materials systems, once disseminated, should also spur advances in related areas of catalysis and separations.

Perhaps the broadest benefit to the materials community, and the greatest challenge, would be completely predictive *in silico* design. Such a strategy would have broad and profound implications for the state of our general knowledge of materials discovery, synthesis, and processing. For example, systematic studies of materials could lead to information on trends that expose new relationships between changes in properties and a concomitant variation in chemical structures. This information is destined to be more useful than simply discovering a particular material, as it is likely to spur the foundation of new theories and models describing the composition of chemical space, as well as describing composition/function relationships. Such theories and models can be applied quite generally to discover other types of materials beyond the scope of this report and its emphasis on O_2 and CO_2 separation applications.

Discovery of novel materials and their refinement for a specific separation process is, at its heart, an optimization problem. Optimization requires knowledge of targets and setpoints.

The targets (e.g., selectivity, capacity) need to be more clearly defined, and there is a significant impetus to define standardized tests and metrics to assess the performance of candidate structures. This will ensure that the scientific community has not only a common goal to achieve but also a readily available measure of progress toward it.

Inverse design and the computational prediction of new structures could open completely new avenues for discovery of carbon capture materials. The excitement of these "high-risk, high-gain" approaches lies in their potential to move the scientific community beyond continued study of perturbations of known materials toward a disruptive technology capable of leading to dramatically different suggestions for materials, synthesis techniques, and processing conditions to answer the looming carbon capture problem.

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CONCLUSION

CONCLUSION

The scientific basis for our understanding of the impacts of increased atmospheric CO_2 on the climate and the environment has developed dramatically since 1896, when Svante Arrhenius published a paper entitled, "On the Influence of Carbonic Acid in the Air upon the Temperature of the Ground."[1] We now understand at a deep level how increased atmospheric CO_2 influences the radiative fluxes that influence the surface temperature of our planet, and our understanding of the feedback mechanisms and fingerprints associated with CO_2-driven climate change continues to grow into a definitive body of evidence. Since the time of Arrhenius, the mass of CO_2 released to the environment annually has increased to more than 30 Gt (30 billion tonne) and the impacts of these emissions to the global environment are well documented. Yet the problem continues to increase annually, with CO_2 emissions expected to grow by 40% by 2035 as the populations in countries with growing economies increase and the demand for energy continues to rely on combustion of carbon-based fuels for industry, transportation, and residential use.

Even with the development of renewable energy sources and expanded use of nuclear energy, the world's demand for electric energy will still be dependent on carbon-based fuels for the near future. Today's demand of 20 trillion kWh of electricity is projected to increase to over 35 trillion kWh by 2035, while the portion coming from combustion processes is projected to decrease only by about 10% as new renewable and nuclear power generation capabilities come on line.[2] To decrease CO_2 emissions in the future will clearly require even more substitution of non-carbon-based sources of electricity; however, for the foreseeable future, the efficient capture of CO_2 is a necessary part of the solution to the carbon emission problem.

The magnitude of this challenge is daunting. A typical 550 MW coal-fired electrical plant produces about 2 million ft^3 of flue gas *per minute,* containing a mixture of CO_2, H_2O, N_2, O_2, NO_x, SO_x, and ash. However, the CO_2 is present at very low concentrations (<15%) after conventional combustion, requiring very effective separation processes. Precombustion strategies, in which coal is gasified prior to combustion, can be used to increase the concentration of CO_2 in the flue gas to about 40%. An especially promising strategy is to use oxycombustion, whereby purified oxygen (separated from air) is used in the combustion process, and the concentration of CO_2 is increased to over 60% in the resulting emission. Today, the cost of capturing CO_2 is high, adding an estimated 30% or more to the cost of electricity depending upon the process employed.[3] Much energy is spent on releasing and regenerating the capture media in the case of solid adsorbents and liquid absorbents, or on maintaining pressure/temperature drops to drive membrane-based separations. Moreover, while current technologies are relatively efficient overall, it is difficult to scale them to the levels required at a large electrical generation facility. Thus new carbon capture strategies are critically needed for the efficient, cost-effective reduction of CO_2 emissions.

The workshop "Carbon Capture: Beyond 2020" was sponsored by the DOE Offices of Basic Energy Sciences and Fossil Energy with the goal of assessing the current state of the art in carbon capture technologies and projecting fundamental research needed to meet future needs in carbon capture. This workshop followed a previous workshop, "Carbon Capture

2020," which focused on near-term strategies for carbon capture improvements (http://www.netl.doe.gov/publications/proceedings/09/CC2020/pdfs/Richards_Summary.pdf.

Before "Carbon Capture: Beyond 2020," an in-depth assessment of technologies for carbon capture was conducted, and a factual document, *Technology and Applied R&D Needs for Carbon Capture: Beyond 2020*, was prepared to identify technical bottlenecks that need to be addressed by basic research (see Appendix A). As a result, the workshop considered the separation processes needed for three CO_2 emission reduction strategies—postcombustion, precombustion, and oxycombustion—and assessed three primary separation technologies based on liquid absorption, membranes, and solid adsorption. Although precombustion and oxycombustion methods are less challenging from the perspective of capturing CO_2, they require the construction of new plants or retrofitting of existing plants, respectively. Postcombustion capture may use decades-old technology, but it remains far from meeting the huge demands for reduction of carbon emissions.

This goal of this workshop was to think beyond current technologies, to address the identified technical bottlenecks from a different perspective—one from which entirely new concepts for separation technologies could be based in 2020 and beyond. In addressing these issues, the workshop attendees realized that the technical challenges facing next-generation carbon capture processes are immense. However, they also noted that the recent advances in nanoscience, characterization tools, and computational tools provide an unprecedented opportunity to understand the chemical and physical processes involved in gas separations at the atomic and molecular levels. Understanding the fundamental principles of these processes was identified as a critical requirement for designing new materials and chemical processes upon which revolutionary separation processes could be based. This knowledge can be obtained only through fundamental research and could lead to a new generation of efficient and cost-effective separation processes. For example, one could even envision tailored materials that could manipulate molecular species and even respond to external stimuli to minimize the total energy needed for effective capture and release.

This report summarizes the technical challenges identified at the workshop and outlines a number of Priority Research Directions (PRDs) that would address current technical bottlenecks in carbon capture technologies. These high-level PRDs are meant to inspire researchers as they formulate research strategies to develop new materials and chemical processes for carbon capture. One major theme of the workshop was centered on understanding the interaction of the targeted species with the separation media. These interactions can be weak or strong, but they need to be understood and controlled at the nanoscale to allow efficient uptake, transport, and release. They occur on surfaces (e.g., particles), at interfaces, or in confined spaces (e.g., pores) and can be hugely affected by surface functionalities and local environments. Compounding the challenge of understanding these atomic and molecular interactions is the fact that the processes occur far from equilibrium and under extreme conditions. Fundamental knowledge is required to allow these interactions to be designed and controlled with high specificity rather than optimized by simple trial and error. It was noted that while the understanding of materials at the interface of gases/liquids with solids has progressed recently, far less is known about solute/liquid interactions found in liquid absorption separation processes, representing a particularly significant scientific challenge.

A second major theme of the report builds on the first theme of understanding gas/media interactions and centers on the discovery and design of new materials for separations. Several PRDs are focused in this area and seek to develop new ways to control the structure and functionality of materials to effect highly efficient separation processes. Achieving new classes of materials that take advantage of the enabling features of atomic/molecular architecture, structural dynamics, and physical/chemical phenomena to maximize selective mass transport is a scientific grand challenge. Of particular interest would be the ability to design and synthesize materials with controlled structure in three dimensions on multiple length scales (e.g., from nanometer to micron). These same capabilities would open up the ability to incorporate features that increase the stability of materials or even "self-repair." The required advances in design and synthesis span broad classes of materials—including polymer and inorganic membranes, inorganic solids, fluids and hybrid composites. Taking advantage of nanoscale design and control, these materials could be synthesized using top/down, bottom/up, or even self-assembly techniques. Further, they could be designed to incorporate cooperative processes to enhance selectivity, similar to processes that occur in nature. This could be accomplished by coupling the binding of a target gas with a change in a structure or other change in the capture material to lower the overall energy cost of the coupled uptake and release process. The ability to control structure and functionality of materials opens up unprecedented capabilities for maximizing uptake, transport, and release of target gases.

A third major theme in the report involved the need to develop innovations in the triggers that are used to drive capture/release processes. Today's gas separation processes typically use changes in pressure or temperature (so-called "swings") to drive separations, which give rise to increased energy requirements. To realize more effective means of capturing and releasing carbon dioxide, alternative triggers are critically needed to make future separation process more cost effective. To harness these alternative driving forces will require the design of "smart" materials that have switchable behaviours that can be triggered by external forces. For example, a material might be designed that could be switched between an open phase to allow gas transport and a closed phase to capture targeted species. Such smart materials are known in nature, including channels in cell membranes that allow the selective transport of ions and small molecules. The triggers for such changes could be manifested in any number of forms, including light, electric and magnetic fields, and chemical gradients or pH, among others. Designing materials that are driven by energy effective triggers will require understanding the structure/performance relationships of these separations systems at the molecular level. This understanding will drive the development of radically different separation schemes, including the possible application of a combination of driving forces in multi-functional separation materials.

As emphasized throughout the Report, to design new classes of separation materials with tailored properties requires the fundamental understanding of the myriad physical and chemical processes that affect a particular separation scheme. Thus, a major cross-cutting research theme identified in the Report was the development of analytical tools that can characterize materials structure and molecular processes across broad spatial and temporal scales. Specific needs identified in the Report include examining interfaces and thin films at the atomic and molecular levels, achieving an atomic/molecular-scale understanding of gas-host structures and kinetics, and understanding and controlling nanoscale synthesis in multiple dimensions. The Report outlines the need for new capabilities to enable the study of processes involved in carbon capture processes under realistic conditions, which include extreme, dynamic conditions (e.g., T, P and others).

It was also recognized that state-of-the-art characterization tools need to be integrated in a way that the resulting data can be assembled to guide interpretation and modeling of experiments. Such multi-dimensional analytical information will revolutionize the way experiments are conducted and expedite the discovery of new materials and processes for carbon capture. Further, to achieve an atomic and molecular understanding of structure and chemical processes, a particularly challenging need is the ability to develop analytical tools that can recognize unique events rather than the ensemble response that is most often measured using today's analytical tools. Further, new measurement techniques need to be able to examine the dynamics of binding events, and to be able to selectively examine interfaces, be they flat or internal. The advent of new spectroscopic tools and the continue support of photon and neutron science facilities is thus a critical element.

Another major cross-cutting theme focused on the need for new computational tools. These tools were recognized as critical components in an integrated approach, along with synthesis and characterization, to achieve the research goals outlined throughout the Report. Computer simulation techniques, from ab initio to continuum-based approaches are needed to predict solutions for carbon capture scenarios. These predictions can be used to direct experimental studies of specific candidate materials and processes for carbon capture. New algorithms that form the basis of "inverse design" will play a key role in the expansion of computer simulation and modeling for carbon capture processes. The development of improved simulation techniques and coarse-grained models to handle mixture adsorption and diffusion inside complex materials will have a significant influence on the way adsorption and diffusion are modeled. Computational tools will also provide advanced capabilities for interpreting experimental results, revealing mechanisms, predicting trends and guiding additional experiments.

With the continued dependence on combustion of carbon-based fuels for the foreseeable future, there is an urgent need to devise new separation methods to minimize the emission of CO_2 to the environment. The vast quantities of gases that must be managed in carbon capture processes presents a huge challenge and the workshop panelists readily realized that today's technologies for separation of targeted gases from a complex fall far short of meeting this challenge because of limits in efficiencies and costs. It was clear that while some improvements could be made by optimizing today's processes, wholly new concepts are needed to meet the full requirements of carbon capture for the future. To realize these new concepts requires developing an atomic- and molecular-level understanding of the many physical and chemical processes that occur in gas separations. Only with this fundamental knowledge will we be able to break through the limitations of today's carbon capture technologies. Armed with this knowledge, new materials and chemical processes to capture and release target molecules with vastly improved efficiencies can be developed and incorporated into new separations technologies.

The research needs outlined in this Report represent some of the most challenging areas in science today—understanding interfaces (gas/liquid/solid), designing materials with specific architectures and functions, and achieving materials that respond to an external stimulus as commonly occurs in nature. However, the workshop panelists were confident that the challenges confronting carbon capture could be met with fundamental research that takes advantage of recent advances that have been made in synthesis, characterization and computation. Specifically, these challenges will require the use these three capabilities synergistically to observe, understand, predict, and design revolutionary new materials that are specifically tailored for highly efficient separations. The panelists also recognized that these challenges will require the concerted efforts of research teams composed of materials scientists, chemists, physicists, computational scientists, engineers and other disciplines to realize the required breakthroughs. In addition, these efforts will require close collaborations between fundamental science and applied science to provide feedback and guidance to realize the full potential of harnessing the breakthroughs and translating them into large scale carbon capture technologies. Finally, the workshop panelist were highly confident that, with concerted effort, future technologies for dramatically reducing carbon emissions to the environment could be achieved, but noted that this goal will require substantial investment in fundamental research.

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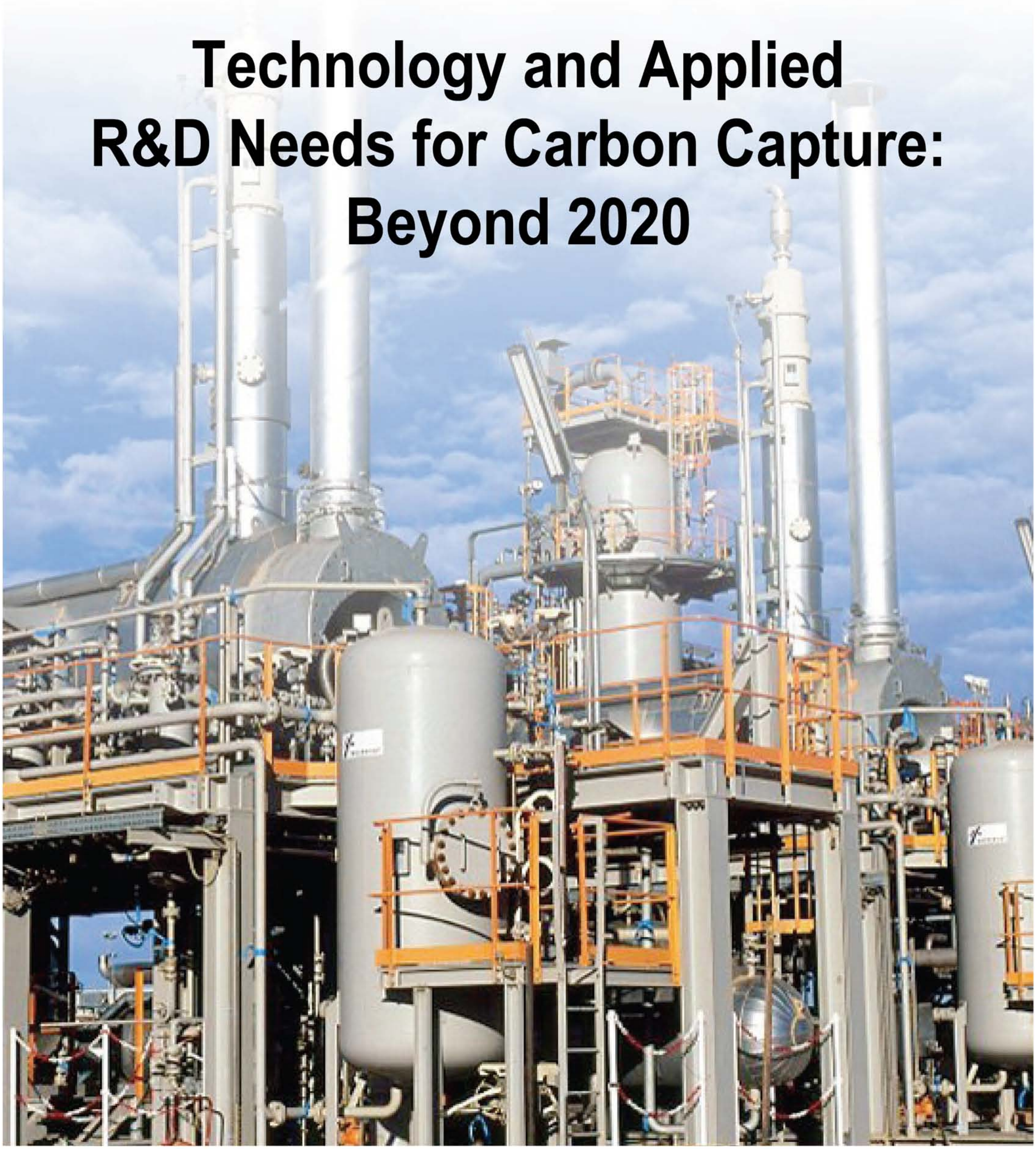
APPENDIX A: TECHNOLOGY AND APPLIED R&D NEEDS FOR CARBON CAPTURE BEYOND 2020

Technology and Applied R&D Needs for Carbon Capture: Beyond 2020



Resource Document for the Workshop on Carbon Capture: Beyond 2020

March 2010

On the cover:

An amine-based CO_2 capture system used to purify natural gas at BP's In Salah plant in Algeria. Approximately 1 Mt/year of CO_2 is captured and transported by pipeline to a geological sequestration site. (Photo courtesy of IEA Greenhouse Gas Programme).

TECHNOLOGY AND APPLIED R&D NEEDS FOR CARBON CAPTURE: BEYOND 2020

Resource Document for the Workshop on Basic Research needs for Carbon Capture: Beyond 2020

March 2010

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CONTENTS

ABBREVIATIONS, ACRONYMS, AND INITIALISMS

ASU	air separation unit
bmim	1-butyl-methylimidazolium
Btu	British thermal units
CAP	chilled ammonia process
CCS	carbon capture and storage
CHA	chabazite
CLC	chemical looping combustion
CLG	chemical looping gasification
CO_2	carbon dioxide
COE	cost of electricity
dca	dicyanamide
DDR	Deca-dodecasil 3R
dhtp	2,5-dihydroxyterephthalate
DOE	Department of Energy
emim	1-ethyl-3-methylimidazolium
EOR	enhanced oil recovery
EPRI	Electric Power Research Institute
FAU	faujasite
GPU	gas permeation unit
hmim	1-hexyl-3-methylimidazolium
hmpy	1-hexyl-3-methylpyridinium
IGCC	integrated gasification combined cycle
IL	ionic liquid
IM	imidazolate
MEA	monoethanolamine
MFI	mordenite framework inverted
MHI	Mitsubishi Heavy Industries
MOF	metal-organic framework
MW	megawatt
MWH	megawatt hours
NCCC	National Carbon Capture Center
NETL	National Energy Technology Laboratory
NGCC	natural gas combined cycle
PC	pulverized coal
PES	polyethersulfone
PSA	pressure-swing adsorption
PSDF	Power Systems Development Facility
PSF	polysulfone
psia	pounds per square inch absolute
PZ	piperazine
SC	supercritical
SLM	supported liquid membranes
SNG	substitute natural gas
SubC	subcritical
tdtdp	trihexyltetradecylphosphonium
Tf_2N	bis(trifluoromethylsulfonyl)imide
USC	ultrasupercritical
WGS	water-gas shift
ZIF	zeolitic imidazolate framework

1.0 Introduction

A large body of evidence demonstrates that global temperatures are rising. Eleven of the past 12 years rank among the 12 warmest since the 1850s, when temperature began to be regularly recorded [1]. Many attribute this recent global warming to human influence on atmospheric composition, particularly the increase in carbon dioxide. Over the past several hundred years, atmospheric CO_2 concentrations have steadily increased from the pre-industrial level of 280 to over 370 ppm. The increases in CO_2 concentrations are attributed primarily to burning of coal, oil and natural gas for electrical generation, transportation, industrial and domestic uses (e.g. cement manufacturers). In 2007, human activities emitted roughly 37 $GtCO_2$ to the atmosphere, 85% of which came from combusting fossil fuels as a primary energy source and the balance from changes in land cover [2, 3]. Roughly one-third of the 37 $GtCO_2$ emitted in 2007 came from the United States and China [4]. If unabated, atmospheric CO_2 levels will continue to increase rapidly and, within 50 years, may exceed concentrations needed to protect sensitive ecosystems and avoid flooding in low-lying coastal areas. To address this challenge, a multi-pronged approach is needed to decrease CO_2 emissions which include efficient production and use of energy, solar power, wind energy, biomass utilization, switching to fuel sources with lower or negligible emissions, and carbon capture and storage (CCS).

Carbon capture involves the separation of CO_2 from an effluent stream and compressed to a liquid or supercritical state for transportation by pipeline. It is then injected into geologic reservoirs (e.g., oil and gas fields, deep saline aquifers) where the geologic structure and processes are expected to store the CO_2 for thousands of years. CCS is currently high on administrative and legislative agendas worldwide. In July 2008, the G8 leaders called for 20 CCS demonstrations announced globally by 2010. Since then, many countries have invested significant sums to initiate commercial-scale demonstrations and began developing policies to address legal and regulatory concerns about geologic storage. Capture standards for new facilities have been proposed in legislation in Europe and the United States. These proposals would set a performance standard (either in unit of CO_2 per unit of energy or as a percentage-based reduction in overall CO_2 emissions).

In the United States, the majority of 2008 emissions from stationary sources came from the electricity sector, primarily from coal-fired power plants [5]. A wide variety of industrial facilities also emit CO_2 as a by- or co-product of the industrial processes inherent to their industry, such as ethanol fermentation, oil and gas refining, chemical (including ethylene and ethylene oxide) production, hydrogen production, as well as others such as pulp and paper, iron and steel, ammonia and fertilizer, and cement manufacturing. CO_2 in exhaust streams is present to various extents, at various temperatures and pressures, and with various other constituents (e.g. NO_x, SO_2). Such a variety suggests that different markets for CO_2 capture technologies might exist and that number of different technologies to capture CO_2 will be necessary. A cost-effective technology that is flexible and robust to these different applications, however, is likely to be valued and more desirable than a niche-market counterpart.

A typical taxonomy separates CO_2 capture into three categories: (1) post-combustion, (2) pre-combustion, and (3) oxy-combustion capture [5]. Post-combustion capture separates CO_2 from exhaust gases. Using coal as a fuel, pre-combustion capture entails gasifying the coal prior to combustion in a process that produces a readily capture-able stream of CO_2. The technology used for carbon capture in pre-combustion is similar to that used in the hydrogen industry. Oxy-combustion capture produces a relatively pure stream of CO_2 and water vapor by burning the coal in pure oxygen, where nitrogen is separated from air prior to combustion. Processes that seek to capture 90% or more of the CO_2 in the exhaust stream are being developed, but it is equally if not more important that this treated stream be composed as much as possible of the exhaust stream that would otherwise be emitted. The gigatons of CO_2 that need to be captured necessitate the reuse of any capture material. It is further crucial to consider how the capture technology can scale with the exhaust stream and the amount of CO_2 being emitted. Similarly, the physical space needed for the capture technology is important; roughly doubling the size of the facility that produces the CO_2. Furthermore, the potential for retrofits to the old fleet of coal-fired power plants and new-build installations of CO_2 capture technology will vary regionally, and provide incentive for technology development for both retrofits and new-builds. Importantly, current capture systems require large amounts of energy to operate. This decreases net efficiency and contributes significantly to CO_2 capture costs. Depending on the nature of the point source, cost estimates range from as low as roughly \$20/tCO_2 to nearly \$100/tCO_2 [5, 6]. Technological advances driven by multi-disciplinary fundamental research offer a path forward leading to novel materials and processing methods that will greatly improve capture efficiencies and lower cost.

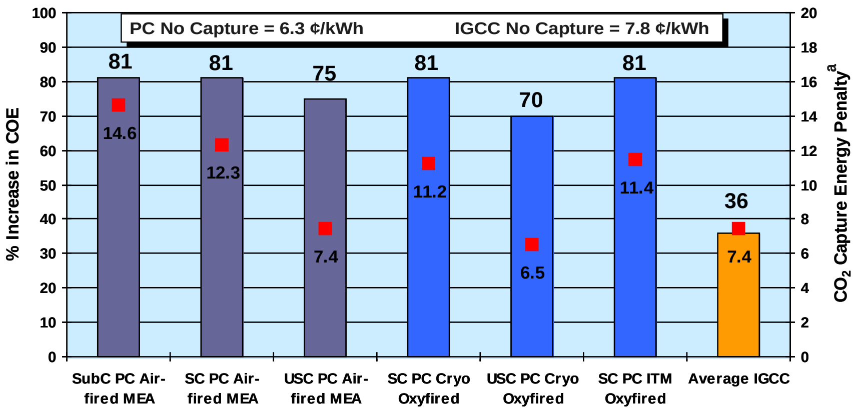
This document provides the factual background for the basic science and research needs for CO_2 capture technologies to support the BES Basic Research Needs Workshop for Carbon Capture: 2020 and Beyond. This workshop will identify key basic research directions that could provide transformative breakthroughs needed for meeting future requirements for carbon capture. The intent of this document is to provide a broad-based overview of current technologies used for carbon capture – focusing primarily on materials used for carbon capture and alternative gas separation pathways – and to better define the requirements necessary to achieve fundamental breakthroughs that propel carbon capture technology into the next decade. This overall reference will not only provide background for participants in the workshop, but also a template for future technology development going forward.

2.0 Carbon Capture Technologies

There are commercially-available CO_2 capture technologies that are currently being used in various industrial applications and being tested for power plant capture in pilot and demonstration projects. However, in their current state of development these technologies are not ready for broad-based implementation on coal-based power plants for two primary reasons: 1) they have not been demonstrated at the scale necessary for power plant application, and 2) if successfully scaled-up, they would not be cost effective at their current level of process development. Other major technical challenges associated with the application of existing CO_2 capture technologies to coal-based power plants include auxiliary power requirements, energy efficiency, energy integration, flue gas contaminants, water use, CO_2 compression, and oxygen supply for oxy-combustion systems. A broad portfolio of research pathways are being investigated in three technology approaches for CO_2 capture – post-combustion, pre-combustion, and oxy-combustion. A key point is that the majority of the technology options being considered are still in the laboratory and bench-scale stage of development.

DOE has conducted systems-analysis studies that show currently available CO_2 capture technologies are expensive and energy-intensive, which would seriously degrade the overall efficiency of both new and existing coal-based power plants [7]. Figure 1 presents the impact of current state-of-the-art CO_2 capture technologies on the normalized cost of electricity (COE) and net efficiency of new coal-based power plants. For example, a subcritical pressure, air-fired power plant equipped with an amine-based solvent CO_2 capture process is estimated to have an 81 % higher COE and 14.6 % lower efficiency than a similar plant without CCS. Three major conclusions can be drawn from the DOE analysis:

- For all CO_2 capture cases, the COE is significantly higher than baseline costs.
- Plant efficiencies are substantially degraded in all processes as a result of large parasitic energy consumption associated with the CO_2 capture.
- It is important to develop new advanced CO_2 capture technologies in order to maintain the cost-effectiveness of U.S. coal-based power generation.



[a] CO_2 Capture Energy Penalty = Percent points decrease in net power plant efficiency due to CO_2 capture compared to Supercritical PC w/o CO_2 capture (39.5%) or average IGCC w/o CO_2 capture (39.5%)

Figure 1. Impact of current state-of-the-art CO_2 capture technologies on the normalized cost of electricity and net efficiency of new coal-based power Plants (PC: pulverized coal; SubC: subcritical; SC: supercritical; USC: ultrasupercritical).

2.1 Post-Combustion CO_2 Capture

Post-combustion CO_2 capture offers the greatest near-term potential for significantly reducing CO_2 emissions since these technologies can be retrofit to the existing fleet of coal-fired power plants, which will likely produce the bulk of coal-fired CO_2 emissions for the foreseeable future. Post-combustion CO_2 capture involves the separation of CO_2 from the combustion flue gas, purification, and compression in preparation for geological storage or beneficial use such as enhanced oil recovery. It is primarily applicable to conventional coal-fired, oil-fired or gas-fired power plants, but could also be applicable to integrated gasification combined cycle (IGCC) and natural gas combined cycle (NGCC) flue gas capture. As shown in Figure 2, in a typical coal-fired power plant, fuel is burned with air in a boiler to produce steam that drives a turbine/generator to produce electricity. Flue gas from the boiler consists mostly of nitrogen, water vapor, and CO_2. Separating CO_2 from this flue gas is challenging for several reasons: a high volume of gas must be treated (~2 million cubic feet per minute for a 550 MW plant); the CO_2 is dilute (between 12 and 14 % CO_2); the flue gas is at atmospheric pressure; trace impurities (particulate matter, sulfur oxides, nitrogen oxides, etc.) and oxygen can degrade chemical scrubbing agents; and compressing captured CO_2 from near atmospheric pressure to pipeline pressure (about 2,200 psia) requires a large auxiliary power load.

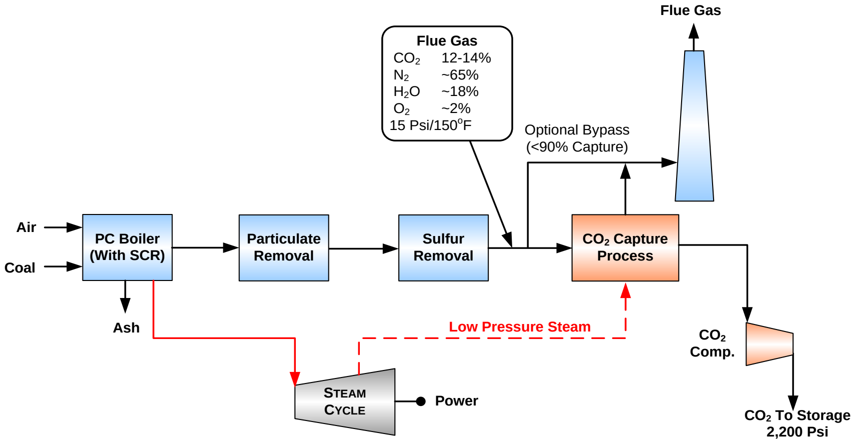


Figure 2. Block diagram illustrating a power plant with post-combustion CO_2 capture.

2.1.1 Currently Available Post-Combustion Capture Technologies

Amine-based chemical solvents, such as aqueous monoethanolamine (MEA), have been utilized for more than 60 years for removal of acid gases (CO_2 and H_2S) from natural gas streams and food-grade CO_2 production. This experience consists of several small (two to 320 ton/day) capacity capture plants that supply CO_2 for the food and beverage industry and a few large (800 to 1,000 ton/day) capture plants that use the CO_2 for enhanced oil recovery (EOR) [8, 9]. MEA scrubbing is capable of achieving high levels of CO_2 capture (90 % or more) for post-combustion applications, but it has not been demonstrated at the larger-scale necessary for coal-fired power plants (e.g., approximately 10,000 tons/day CO_2 production from a 500-MW coal-fired power plant). Although AES's coal-fired Warrior Run and Shady Point power plants are equipped with MEA scrubbers developed by ABB Lummus, they were designed to process a relatively small percentage of the plants' flue gas. At Warrior Run, the MEA system removes CO_2 from only about three to five percent of the flue gas (150 to 200 tCO_2 per day) that is subsequently used for the food processing industry.

Current amine solvents are corrosive; susceptible to degradation by trace flue gas constituents (particularly SO_X); and necessitate significant amounts of energy, in the form of low-pressure steam, for sensible heating, heat of reaction, and stripping for CO_2 regeneration. As shown in Figure 2-1, installing the current state-of-the-art MEA post-combustion CO_2 capture technology on new conventional subcritical (SubC), supercritical (SC), and ultrasupercritical (USC) coal-fired power plants would increase the COE by about 75 to 80 %. Further, the large quantity of energy required to regenerate the MEA solvent would reduce the net efficiency of new SubC and SC coal-fired power plants by more than 12 %.

Amines chemically react with CO_2 via reversible reactions to form water-soluble compounds. Despite the low CO_2 partial pressure in combustion flue gas, amines are capable of achieving high levels of CO_2 capture due to fast kinetics and strong chemical reactions. However, the absorption capacity for today's commercially available amines is chemically limited with two moles amine for each mole of CO_2 being required. In addition, typical amine solution concentrations are limited by viscosity and corrosion. Therefore, current amine systems use a solution that is between 20 and 30 % amine with the balance being water. Although the 70 to 80 % water present in the solution helps control the solvent temperature during the absorption exotherm, the water, with its high heat capacity, necessitates significant amounts of sensible heating and stripping energy upon CO_2 regeneration. Various vendors offer different designs of amine systems. In general, depending on the amount of heat integration, anywhere from ~1,500 to more than 2,000 British thermal units (Btu) per pound of CO_2 captured is required in the form of low pressure steam (approximately 45 psia) to regenerate the solvent to produce a concentrated CO_2 stream at a pressure of approximately 25 psia.

2.1.2 Challenges and Technology Needs in Post-Combustion CO_2 Capture

There are several advanced post-combustion CO_2 capture technologies under development, including processes involving solvents, sorbents, and membranes. Challenges and needs for development of practical technologies are summarized in Table 1 and the paragraphs below.

<u>Liquid Solvents:</u> Post-combustion solvent-based CO_2 capture involves chemical or physical sorption of CO_2 from flue gas into a liquid carrier. Chemical absorption involves one or more reversible chemical reactions between CO_2 and an aqueous solution of an absorbent, such as an alkanolamine (e.g., MEA), hindered amine, aqueous ammonia, or a carbonate, to form water-soluble compounds. Although high levels of CO_2 capture are possible, the drawback of this approach is that significant amounts of energy are required in the regeneration step, which involves a temperature swing to break the absorbent-CO_2 chemical bond. Physical absorption is a bulk phenomenon where inorganic or organic liquids

preferentially absorb a gaseous species from the gas mixture. Physical absorption is being used in smaller-scale industrial applications. Although physical solvent regeneration is less energy-intensive than chemical systems, this technology is considered more practical for processing the high-pressure syngas generated at coal gasification plants since CO_2 solubility in physical solvents increases with partial pressure. Practical challenges in solvent-based CO_2 capture include large flue gas volume, relatively low CO_2 concentration, flue gas contaminants, and high parasitic power demand for solvent recovery. Technology needs include low-cost, non-corrosive solvents that have high CO_2 loading capacity, improved reaction kinetics, low regeneration energy, and resistance to degradation.

Table 1. Post-Combustion Capture Advantages and Challenges

CO_2 Capture Technology	Description	Advantages	Challenges
Liquid Solvent	Solvent reacts reversibly with CO_2, often forming a salt. Solvent is regenerated by temperature swing, which reverses the absorption reaction (normally exothermic). Solvent is often alkaline.	• Chemical solvents provide fast kinetics to allow capture from streams with low CO_2 partial pressure • Wet-scrubbing allows good heat integration and ease of heat management (useful for exothermic absorption reactions)	• Significant amount of steam required to reverse chemical reaction de-rates power plant • Energy required to heat, cool, and pump non-reactive carrier liquid (usually water) is often significant • Vacuum stripping can reduce regeneration steam requirements but is expensive
Solid Sorbent	When sorbent pellets are contacted with flue gas, CO_2 is absorbed onto chemically reactive sites on the pellet by a reversible reaction. Pellets are regenerated by temperature swing, which reverses the absorption reaction.	• Chemical sites provide large capacities and fast kinetics, enabling capture from streams with low CO_2 partial pressure • Higher capacities on a per mass or volume basis than similar wet-scrubbing chemicals • Lower heating requirements than wet-scrubbing in many cases (CO_2 and heat capacity dependant)	• Heat required to reverse chemical reaction (although generally less than in wet-scrubbing cases) • Heat management in solid systems is difficult, which can limit capacity and/or create operational issues when absorption reaction is exothermic • Pressure drop can be large in flue gas applications • Sorbent attrition
Membrane	Uses permeable or semi-permeable materials that allow for the selective transport and separation of CO_2 from flue gas.	• No steam load • No chemicals	• Membranes tend to be more suitable for high-pressure processes such as IGCC • Trade off between recovery rate and product purity (difficult to meet both high recovery rate and high purity) • Requires high selectivity (due to CO_2 concentration and low pressure ratio) • Good pre-treatment • Bad economy of scale • Multiple stages and recycle streams may be required

<u>Solid Sorbents:</u> Solid sorbents, including sodium and potassium oxides, zeolites, carbonates, amine-enriched sorbents, metal organic frameworks (MOFs) and zeolitic imidazolate frameworks (ZIFs), are being explored for post-combustion CO_2 capture. A temperature swing facilitates sorbent regeneration following chemical and/or physical adsorption, but a key attribute of CO_2 sorbents is that less H_2O is present compared to solvent-based systems, thereby reducing the sensible heating and stripping energy requirements. Possible configurations for contacting the flue gas with the sorbents include fixed, moving, and fluidized beds. Challenges in the application of sorbent-based systems include solids circulation, sorbent attrition, low chemical potential, heat transfer, reactive flue gas contaminants, and the parasitic power and potential water demand for sorbent regeneration. Technology needs include low-cost, durable sorbents that have high selectivity, high CO_2 adsorption capacity, and ability to withstand multiple regeneration cycles.

<u>Membranes:</u> The potential of membrane-based CO_2 capture is generally viewed positively for high-pressure applications, such as IGCC, but not as promising for low-pressure combustion flue gas without further process enhancements. Usually, the selectivities of the membranes in one stage are insufficient to achieve the desired purities and recoveries, so multiple stages and recycle may be required in an actual operation, leading to increased complexity, energy consumption, and capital costs. CO_2 membranes could have an advantage if a lower rate of CO_2 removal (<90 %) is acceptable. Practical challenges to the use of membrane-based systems include large flue gas volume, relatively low CO_2 concentration, low flue gas pressure, flue gas contaminants, and the need for high membrane surface area. Technical needs for post-combustion membranes include low-cost, durable membranes that have improved selectivity, thermal and physical stability, and tolerance of contaminants in combustion flue gas.

2.2 Pre-Combustion CO_2 Capture

Pre-combustion capture is mainly applicable to gasification plants, where fuel is converted into gaseous components by applying heat under pressure in the presence of steam and sub-stoichiometric oxygen (O_2). A simplified process schematic for pre-combustion CO_2 capture is shown in Figure 3. By carefully controlling the amount of oxygen, only a portion of the fuel burns to provide the heat necessary to decompose the fuel and produce synthesis gas (syngas), a mixture of hydrogen (H_2) and carbon monoxide (CO), along with minor amounts of other gaseous constituents. To enable pre-combustion capture, the syngas is further processed in a water-gas shift (WGS) reactor, which converts CO into CO_2 while producing additional H_2, thus increasing the CO_2 and H_2 concentrations. An acid gas removal system can then be used to separate the CO_2 from the H_2. Because CO_2 is present at much higher concentrations in syngas (after WGS) than in flue gas and the syngas is at higher pressure, CO_2 capture is less expensive for pre-combustion capture than for post-combustion capture. After CO_2 removal, the H_2 can be used as a fuel in a combustion turbine combined cycle to generate electricity.

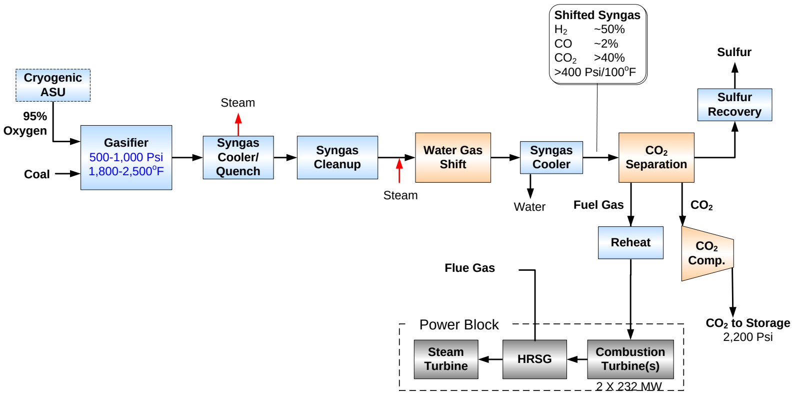


Figure 3. Block diagram illustrating a power plant with pre-combustion CO_2 capture.

2.2.1 Currently Available Pre-Combustion Capture Technologies

The current state-of-the-art CO_2 capture technologies that could be applied to IGCC systems – the glycol-based Selexol™ process and the methanol-based Rectisol® process – employ physical solvents that preferentially absorb CO_2 from the syngas mixture. There are multiple systems in use at commercial scale. For example, a Rectisol® system is used for CO_2 capture at the Dakota Gasification Company's substitute natural gas (SNG) plant located in North Dakota, which is designed to remove approximately 1.5 million tons of CO_2 per year from the synthesis gas. The CO_2 is purified and sent via a 320-km pipeline and injected into the Weyburn oilfield in Saskatchewan. However, this experience is based on a gasification plant, not an IGCC plant. The advantage of physical solvents is that less energy is required in the solvent regeneration step, which involves a temperature increase and/or pressure reduction, leading to an energy penalty of about seven percentage points. Furthermore, although the COE for a base IGCC power plant is higher than a coal-fired plant, the high thermodynamic driving force for CO_2 capture and reduced CO_2 compression demands at IGCC facilities leads to an increase in COE of less than 40 % using Selexol™ technology, compared to 75 to 80 % for a conventional coal-fired power plant equipped with an MEA scrubber for CO_2 control, as shown in Figure 1.

The DOE systems analysis study assumes a WGS reactor combined with a two-stage Selexol™ process is used for CO_2 capture in IGCC applications. The WGS reactor is necessary to convert the CO in the syngas to CO_2. The first-stage Selexol™ process is used for hydrogen sulfide (H_2S) capture, and the second stage for CO_2 capture.

2.2.2 Challenges and Technology Needs in Pre-Combustion CO_2 Capture

There are several advanced pre-combustion CO_2 capture technologies under development, including processes involving solvents, sorbents, and membranes. Challenges and needs for development of practical technologies are summarized in Table 2 and the paragraphs below.

Table 2. Pre-Combustion CO_2 Capture Technology Advantages and Challenges

CO_2 Capture Technology	Description	Advantages	Challenges
Physical Solvent	Solvent readily dissolves CO_2. Solubility is directly proportional to CO_2 partial pressure and inversely proportional to temperature, making physical solvents more applicable to low temperature, high pressure applications (cooled syngas). Regeneration normally occurs by pressure swing.	• CO_2 recovery does not require heat to reverse a chemical reaction. • Common for same solvent to have high H_2S solubility, allowing for combined CO_2/H_2S removal. • System concepts in which CO_2 is recovered with some steam stripping rather than flashed, and delivered at a higher pressure may optimize processes for power systems	• CO_2 pressure is lost during flash recovery • Must cool down synthesis gas for CO_2 capture, then heat it back up again and re-humidify for firing to turbine • Low solubilities can require circulating large volumes of solvent, resulting in large pump loads • Some H_2 may be lost with the CO_2
Physical Sorbent	When sorbent pellets are contacted with syngas, CO_2 is physically adsorbed onto sites and/or dissolves into the pore structure of the solid. Rate and capacity are directly proportional to CO_2	• CO_2 recovery does <u>not</u> require heat to reverse a reaction. • Common for H_2S to also have high solubility in the same sorbent, meaning CO_2 and H_2S capture can	• CO_2 pressure is lost during flash recovery • Must cool synthesis gas for CO_2 capture, then heat it back up again and re-humidify for firing to turbine

	partial pressure, making these sorbents more applicable to high pressure applications. Regeneration normally occurs by pressure swing.	be combined. - System concepts in which CO_2 is recovered with some steam stripping rather than flashed, and delivered at a higher pressure may optimize processes for power systems	- Some H_2 may be lost with the CO_2
H_2/CO_2 Membrane	A membrane material which selectively allows H_2 or CO_2 to permeate, used in gasification operations with concentrated streams of H_2 and CO_2.	H_2 or CO_2 Permeable Membrane: - No steam load or chemical attrition. H_2 Permeable Membrane Only: - Can deliver CO_2 at high-pressure, greatly reducing compression costs. - H_2 permeation can drive the CO shift reaction toward completion – potentially achieving the shift at lower cost/higher temperatures.	- Membrane separation of H_2 and CO_2 is more challenging than the difference in molecular weights implies. - Due to decreasing partial pressure differentials, some H_2 will be lost with the CO_2. - In H_2 selective membranes, H_2 compression is required and offsets the gains of delivering CO_2 at pressure. In CO_2 selective membranes, CO_2 is generated at low pressure requiring compression.
Membrane/Liquid Solvent Hybrids	Flue gas is contacted with a membrane, and a solvent on the permeate side absorbs CO_2 and creates a partial pressure differential to draw CO_2 across the membrane.	- The membrane shields the amine from the contaminants in flue gas, reducing attrition and allowing higher loading differentials between lean and rich amine.	- Capital cost associated with the membrane. - Membranes may not keep out all unwanted contaminants. - Does not address CO_2 compression costs.

Liquid Solvent-Based Processes: Physical solvents are viewed as a potential approach for processing high-pressure, CO_2-rich streams, such as those encountered in IGCC systems that employ an upstream WGS reactor. However, solvent-based processes have several disadvantages, including loss of CO_2 partial pressure during the flash regeneration and requirement of a low operating temperature, thus requiring cooling of the syngas, followed by reheating to gas turbine inlet temperature. Novel, solvent-based processes are necessary that can produce high pressure CO_2 at elevated temperatures.

Potential process improvements include modifying regeneration conditions to recover the CO_2 at a higher pressure, improving selectivity to reduce H_2 losses, and developing a solvent that has a high CO_2 loading at a higher temperature. A physical solvent with acceptable CO_2 capacity at a higher temperature would improve IGCC efficiency.

Solid Sorbent-Based Processes: Pressure-swing adsorption (PSA) is currently used to separate hydrogen from CO_2 and other mixed gas streams. While PSA produces a highly pure hydrogen stream, it does not selectively separate CO_2 from other gases in the stream, and therefore does not produce a pure CO_2 product for storage. Solid sorbents for pre-combustion CO_2 capture from syngas must maintain a high adsorption capacity and be resistant to attrition over multiple regeneration cycles, and exhibit good performance at the high temperatures encountered in IGCC systems to avoid the need for syngas cooling.

Membrane Processes: Membrane-based CO_2 capture uses permeable materials that allow for the selective transport and separation of CO_2 from syngas. Different types of membrane materials are available including polymeric membranes, porous inorganic membranes, palladium membranes, and zeolite membranes. Membrane separation uses partial pressure difference as the driving force and is thus suitable for pre-combustion CO_2 capture. Several barriers must be overcome to reduce the cost and improve the performance of membrane systems. Methods must be found to improve separation and throughput and prevent membranes from becoming less effective over time. Thermal and hydrothermal stabilities of membrane need to be considered. Large-scale manufacturing methods for defect-free membranes and modules must be developed. Better methods are needed to make high-temperature, high-pressure seals using ceramic substrates.

2.3 Oxy-Combustion

Oxy-combustion systems for CO_2 capture rely on combusting coal with relatively pure oxygen diluted with recycled CO_2 or CO_2/steam mixtures. Under these conditions, the primary products of combustion are water and CO_2, with the CO_2 separated by condensing the water. Figure 4 shows the major systems for a power plant equipped for oxy-combustion. Oxy-combustion overcomes the technical challenge of low CO_2 partial pressure normally encountered in coal combustion flue gas by producing a highly concentrated CO_2 stream (~60 %), which is separated from H_2O vapor by condensing the H_2O through cooling and compression. An additional purification stage for the highly concentrated CO_2 flue gas may be necessary to produce a CO_2 stream that meets transportation and sequestration requirements. This purification step should have significantly less cost than a conventional post-combustion capture system due to the high CO_2 concentration and reduced flue gas volume.

However, the appeal of oxy-combustion is tempered by a few key challenges, namely the capital cost and energy consumption for cryogenic air separation unit (ASU) operation, boiler air infiltration that dilutes the flue gas with N_2, and excess O_2 contained in the concentrated CO_2 stream. Flue gas recycle (~70 to 80%) is also necessary to approximate the combustion characteristics of air since currently-available boiler materials cannot withstand the high temperatures resulting from coal combustion in pure O_2. Consequently, the economic benefit of oxy-combustion compared to amine-based scrubbing systems is limited. As shown in Figure 1, construction of a new supercritical (SC) oxy-combustion coal-fired power plant equipped with a commercially-available cryogenic ASU would increase the COE by about 80% and reduce the net plant efficiency by more than 11 % points, as compared to a new SC air-fired, coal-based power plant without CO_2 capture. The parasitic power requirement for cryogenic O_2 production and CO_2 compression alone would increase the COE by nearly 60 %.

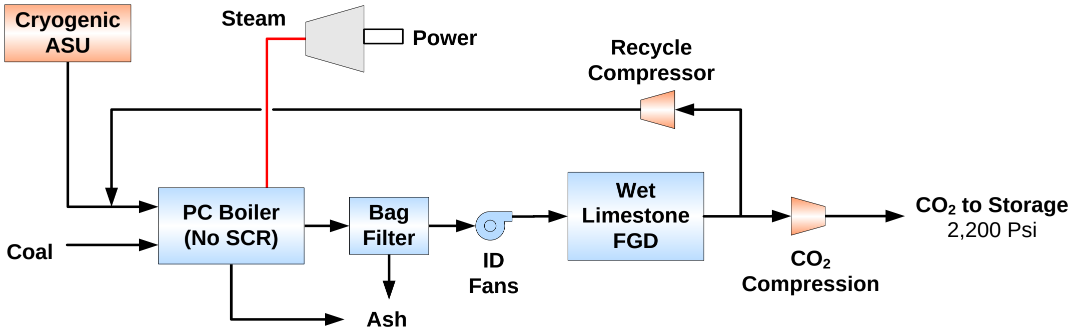


Figure 4. Block diagram illustrating power plant with oxy-combustion CO_2 capture.

2.3.1 Chemical Looping Combustion

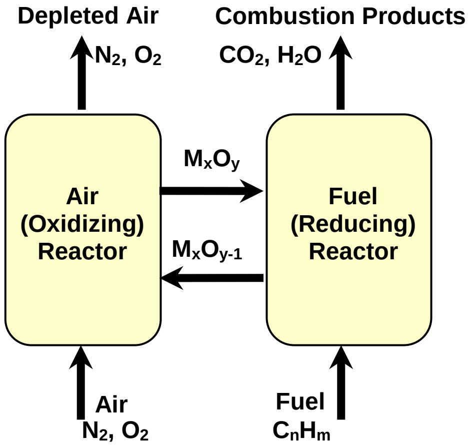


Figure 5. Schematic of chemical looping combustion process.

Chemical looping combustion (CLC) is an advanced coal oxy-combustion technology that involves the use of a metal oxide or other compound as an oxygen carrier to transfer O_2 from the combustion air to the fuel, avoiding direct contact between fuel and combustion air, as shown in Figure 5.

The products from combustion (CO_2 and H_2O) are kept separate from the rest of the flue gases. Chemical looping splits combustion into separate oxidation and reduction reactions. In one potential configuration, chemical looping is carried out in two fluidized beds. The metal oxide (e.g., iron, nickel, copper, or manganese) releases the O_2 in a reducing atmosphere and the O_2 reacts with the fuel. The metal is then recycled back to the oxidation chamber where the metal oxide is regenerated by contact with air. The advantage of using the CLC process is that the CO_2 is concentrated once the H_2O is removed and not diluted with N_2 gas. Another advantage of CLC is that no separate ASU is required and CO_2 separation takes place during combustion.

A related area of research is chemical looping gasification (CLG). In this system, two or three solid particle loops are utilized to provide the O_2 for gasification and to capture CO_2. A loop, similar to that of CLC, is used to gasify the coal and produce syngas (H_2 and CO). A second solid loop is used in a WGS reactor. In this reactor, steam reacts with CO and converts it to H_2 and CO_2. The circulating solid absorbs the CO_2, thereby providing a greater driving force for the WGS reaction. The CO_2 is then released in a calcination step that produces nearly-pure CO_2 for further compression and sequestration.

2.3.2 Challenges and Technology Needs in Oxy-Combustion

Oxy-Combustion: The characteristics of oxy-combustion have not yet been fully developed. Oxy-combustion flame characteristics, burner and coal-feed design, and analyses of the interaction of oxy-combustion products with boiler materials are all areas in need of more research. In addition, because oxy-combustion produces a high- CO_2 flue gas that contains H_2O, excess O_2, N_2, SO_2, NO_X, Hg, and other contaminants, flue gas purification technologies are needed. Companies such as Air Products are currently developing cryogenic purification schemes to remove these contaminants [10]. For oxy-combustion and IGCC to be cost-effective power generation options, a low-cost supply of pure O_2 is required. Although a cryogenic ASU can be used to supply high-purity O_2 to the boiler or gasifier, this commercially-available technology is both capital and energy intensive. Novel production technologies are needed to reduce the cost of O_2 production.

Chemical Looping Combustion and Gasification: Both CLC and CLG are in the early stages of process development [11]. Bench and laboratory-scale experimentation is currently being conducted. Projects in this pathway are advancing the development of chemical looping systems by addressing key issues, such as solids handling and O_2 carrier capacity, reactivity, and attrition. Table 3 provides a summary of the technical challenges for chemical looping technologies.

Table 3. Oxy-Combustion Advantages and Challenges

CO_2 Capture Technology	Description	Advantages	Challenges
Oxy-Combustion	Fossil fuel is combusted with pure oxygen diluted with recycled fuel gas. The combustion product is primarily CO_2 and water.	• The combustion products are CO_2 and water. The relatively pure CO_2 is easily separated thus making the sequestration process less expensive.	• Low cost oxygen supply is required. Currently very high cost. • High cost of CO_2 recycle • Develop processes to convert existing air fired furnaces to oxygen fired. • High temperatures can degrade boiler materials • Requires high temperature materials in new construction
Chemical Looping	Uses metal oxide or other compound as an O_2 carrier to transfer O_2 from the combustion air to the fuel, avoiding direct contact between fuel and combustion air.	• CO_2 and H_2O kept separate from the rest of the flue gases • ASU is not required and CO_2 separation takes place during combustion.	• Undeveloped technology still conceptual and bench scale • Ash separation is problematic • Attrition-resistant metal oxide carriers required during multiple cycles

2.4 Cyrogenic Separation

Cryogenic separation utilizes the attributes of a relatively clean flow stream where all flue gases except N_2 and CO_2 have been removed prior to cooling [12]. This process aims at setting the operational conditions at the triple point of CO_2 (-56.6 °C and 5.17 bars) so that CO_2 will condense while N_2 remains a gas. Once all of the other gases and particulates have been completely removed, the remaining gas is transported to a cryogenic vessel where the temperature and pressure are changed in such a way as to cause CO_2 to liquefy leaving N_2 as a gas. This process allows the N_2 to escape through an outlet at the top of the cryo-vessel while the highly concentrated liquid CO_2 can be collected at the bottom. A similar method commonly termed “refrigeration under pressure” also produces CO_2 from a mixture with N_2 but uses more intense pressurization and somewhat higher temperature compared to cryogenic distillation.

Cyrogenic separation (distillation) has one distinct advantage over most other separation processes; its product is liquid CO_2, which is ready for transport via pipeline or tanker for storage. In addition to being ready for transport, the CO_2 recovery is very high (CO_2 purity after distillation can exceed 99.95%). The cryogenic process is however very energy intensive, wherein the energy required to keep the system cool (commonly using liquid N_2), makes the current process cost ineffective. The other limitation is that NO_x, SO_x, H_2O and O_2 must all be removed from the flue gas prior to cryo-processing. Refrigeration under pressure offers many of the same benefits to cryogenic separation, with similar drawbacks. The cost for cooling under pressure is lower, but more energy is required to pressurize the gases.

2.5 Status of CO_2 Capture Technology Field Testing

2.5.1 Amine-Based Solvent Processes.

With the potential of large-scale power plant CO_2 mitigation on the horizon, technology developers have begun to develop advanced next generation amine solvents. Two leading developers are Fluor

Corporation, with the development of the Econamine FG Plus^{SM} technology, and Mitsubishi Heavy Industries (MHI), with the development of a line of hindered amines and structured packing [13, 14] The optimizations are focused primarily on extensive thermal integration of the CO_2 capture plant with the power plant and the development of improved solvent formulations with lower stripping steam requirements and lower solvent circulation rates than MEA. The following are some examples of the design improvements:

- Improved solvents (higher reaction rates, higher CO_2 capacity, and lower corrosion and degradation).
- Split flow configuration (flash regeneration and steam stripping).
- Absorber intercooling (higher reaction rates, smaller absorber size, lower rich solvent loading).
- Integrated steam generation.
- Structured packing (lower pressure drop and smaller absorber size).

It is important to point out that these technology improvements are still in the development stage and have yet to be demonstrated at power plant scale. To date, no commercial scale of Econamine FG Plus^{SM} plants are operating, but it is being offered commercially by Fluor. A commercial 160 ton/day CO_2 capture plant using MHI's KS-1 technology has been in operation since 1999 at the Petronas Fertilizer Corporation in Malaysia, where the CO_2 is captured from reformer flue gas [8, 9] MHI is currently conducting pilot-scale, slip-stream testing (~10 ton/day CO_2 capture) at a coal-fired power plant in Matsushima, Japan. MHI's next step is to conduct full-scale testing (~500 ton/day CO_2 capture) demonstration at a coal-fired power plant.

2.5.2 Aqueous Ammonia-Based Solvent Processes.

In addition to various chemical amines, aqueous ammonia can be used as a solvent for CO_2 capture that relies upon a temperature swing to cycle between ammonium carbonate and ammonium bicarbonate. This has a significantly lower heat of reaction than amine-based systems, resulting in energy savings, provided the absorption/desorption cycle can be limited to this mechanism. Ammonia-based absorption has other advantages over amine-based systems, such as the potential for high CO_2 capacity, lack of degradation during absorption/regeneration, tolerance to O_2 in the flue gas, low cost, and potential for regeneration at high pressure. Alstom [14] developed the chilled ammonia process (CAP), in which the flue gas is cooled to less than 20°C to optimize the ammonium carbonate reaction with CO_2 and minimize ammonia slip. The resultant ammonium bicarbonate precipitates out of solution as a solid and is subsequently heated to approximately 80°C in the regenerator where the CO_2 is liberated. The ammonia carbonate is then recycled back to the absorber.

An ammonia solvent-based CO_2 capture process [Yeh and Pennline, U. S. patent 7,255,842, August 14, 2007] recently licensed by Powerspan Corporation (ECO$_2^{TM}$) does not require additional flue gas cooling. Therefore, the process operates at a slightly higher temperature than the CAP process and the ammonium bicarbonate remains in solution. Ammonia slip is controlled via integration of the ECO$_2^{TM}$ process with the ECO^{TM} multi-pollutant control system. Powerspan is currently conducting a 1-MW pilot test at FirstEnergy's R.E. Burger Power Station in Ohio.

2.5.3 National Carbon Capture Center. The DOE Office of Fossil Energy, EPRI, and Southern Company are responding to the need for developing cost-effective CO_2 capture technology for coal-based power generation with the addition of the National Carbon Capture Center (NCCC) at the Power Systems Development Facility (PSDF). The PSDF is an engineering-scale demonstration site for advanced power system components located adjacent to Alabama Power's coal-fired Plant Gaston in Wilsonville, Alabama. The PSDF-NCCC can test multiple projects in parallel with a wide range of test equipment sizes leading up to pre-commercial equipment sufficient to guide the design of full commercial-scale power plants. The PSDF-NCCC will be capable of testing pre-, post-, and oxy-combustion technologies.

The backbone of the pre-combustion CO_2 capture technology development will be a high-pressure flexible facility designed to test an array of solvents and contactors. For R&D projects that have been successfully tested at bench-scale in a research lab, the PSDF-NCCC will provide a 1,000 lb/hr flue gas slipstream for screening tests. For technologies that have been successfully tested at the screening-scale, two pilot test beds have been designed, a 5,000 lb/hr (0.5-MW equivalent) slipstream and a 10,000 lb/hr (1.0-MW equivalent) slipstream.

3.0 Materials for Carbon Capture

CO_2 capture systems use many of the known technologies for gas separation which can be integrated into the basic systems for CO_2 capture highlighted in Section 2. Much of this technology centers on the sorptive or separation properties of liquid solvents, solid sorbents or membranes. The state of our knowledge and technologic needs for each of three areas are summarized in this section.

3.1 Liquid Absorbents

The idea of separating CO_2 from flue gas started in the 1970s – not out of concern about greenhouse gas emissions but as a source of potential economically valuable CO_2, mainly for enhanced oil recovery. Taking a cue from industries that needed to remove acid gas impurities (e.g. H_2S and CO_2) from their flow steam, the power industry started to explore the use of chemical adsorbents, specifically monoethanolamine (MEA) solvent, to capture CO_2. MEA is an organic chemical belonging to the family of compounds known as amines. As the first technology of choice for CO_2 capture, amine scrubbing was evaluated in 1991 [16] and was deemed to have unacceptable energy use and costs (materials cost; energy penalty due to water usage and regeneration processing). However, it had been successfully applied to gas [17] and coal-fired plants [18] at a small scale in the early 80s. Despite the cost and inefficiency, amine scrubbing is now a key technology for post-combustion capture. It is expected that new coal-fired power plants may also use post-combustion CO_2 capture by amine scrubbing with ultrasupercritical boiler cycles. Therefore intensive research on the fundamental materials and processes of that build upon amine chemistry will provide a certain, large, payoff.

3.1.1 Amine Scrubbing

CO_2 removal by absorption/stripping with aqueous amine is well-understood and heavily used. A continuous scrubbing system is used to separate CO_2 from a gaseous stream. The system consists of two key components, an absorber in which the CO_2 is absorbed into a solvent, and a regenerator (or stripper), in which CO_2 is released in concentrated form and the original solvent is recovered [19]. CO_2 is absorbed from a fuel gas or combustion gas near ambient temperature into an aqueous solution of amine with low volatility. The amine is regenerated at 100–120 °C by stripping with water vapor produced in a steam-heated reboiler. The hot lean solution is used to preheat the cold rich solution in a cross-exchanger. Water is condensed from the stripper vapor leaving pure CO_2. Chemical absorption systems tend to be more efficient than physical absorption systems because the process is accompanied by a chemical reaction that enhances the overall mass transfer from the initial gas phase to the liquid phase. Despite the cost and inefficiency, currently hundreds of power plants remove CO_2 from natural gas, hydrogen, and other gases with low oxygen. In CCS, the CO_2 would be captured and compressed to 100–150 bar for geologic sequestration.

The process chemistry is complex, but the main CO_2 absorption reaction taking place is given as [20]:

$$\underset{\text{(MEA)}}{2R\text{–}NH_2} + CO_2 \rightarrow \underset{\text{(carbamate)}}{R\text{–}NH\text{–}COO^-} + R\text{–}NH_3^+$$

MEA regeneration involves the application of heat to the products formed in this reaction to liberate CO_2 leaving MEA as a product. There is a sizeable energy penalty for the heat required to regenerate the solvent because substantial energy is needed heat the water/amine solution and break bonds in the carbamate. This heat requirement significantly reduces the net efficiency of the power plant. Pure MEA (with R = HO – CH_2CH_2) is an unhindered amine that forms stable carbamate; hence, only half a mole of CO_2 is absorbed per mole of amine, as depicted in this reaction. For hindered amines (where R is a bulky group; e.g. KS-1), the carbamate formed is not stable, and an alternate reaction leads to higher theoretical capacity of one more of CO_2 per mole of amine [21, 22].The drawback is that CO_2 uptake via hindered amines is very sluggish.

3.1.2 Challenges and Technology Needs in Amine Absorption

Further development of this technology will provide more efficient systems to reduce energy cost, large single absorbers, heat exchangers, and compressors to reduce capital cost, and more robust solvents to reduce makeup costs and secondary environmental impact. MEA processing of CO_2 offers a number of distinct advantages including (a) easy retrofitting – i.e. end-of-the-pipe treatment, (b) effective for dilute CO_2 streams between 3 and 15%, (c) functions well at ordinary temperature and pressure power plant conditions, (d) produces a high-purity reaction product - >98%, and (e) is commercially available [19]. The disadvantages include the substantial energy penalty due to the heat required to regenerate the solvent, loss of solvent due to physical losses, entrainment, vaporization, chemical degradation, and corrosion particularly when O_2 content are high.

Research opportunities leading to improved amine solvents exhibiting better energy performance may be realized by targeting key issues related to their physicochemical properties:

1. Greater thermal stability of the solvent will permit solvent regeneration at greater temperature and pressure. Alkanolamines and other hydrophilic amines typically degrade at 120–130 °C. Cyclic aliphatic diamines such as piperazine are stable up to 150 °C. Other useful structures could be identified that are thermally stable.
2. Greater capacity will reduce the inefficiency of heating and cooling the solvent. Greater solvent concentration increases capacity but also increases viscosity which increases the cost of the cross exchanger. Greater capacity can be achieved by manipulating the volume of CO_2 to volume of absorber ratio. Anhydrous solvents are probably not practical because there is always water in these systems.
3. Greater CO_2 absorption/desorption rates will allow smaller driving force and more reversibility in the absorber. Piperazine provides the fastest rate of the known amines. Other amine structures or enzymes could be used to accelerate CO_2 absorption.

Reduced capital and energy costs will come with amines other than MEA, but there cannot be major improvements since the existing designs already provide about 50% thermodynamic efficiency. Concentrated piperazine (PZ) is a thermally-resistant solvent with a high heat of CO_2 absorption that claims to reduce power loss to 0.24 MWH/tCO_2 by operating the stripper at 150° C. [23] Vacuum stripping or solvents with a lower heat of absorption will not get the full impact of thermal swing stripping and will require more energy [23] Solvents with greater capacity, such as KS-1, minimize sensible heat losses from heating and cooling the circulating solvent. Solvents with a faster rate of CO_2 absorption, such as methyldiethanolamine/PZ, allow for adequate absorber performance with more dissolved CO_2 in the rich and lean solvent, resulting in reduced energy use by the stripper [23].

Improved solvent systems must have low makeup cost, reliable operating characteristics, and minimum impact on the environment. These objectives may be satisfied by meeting these criteria:

1. Slow rate of thermal and oxidative degradation with nontoxic, easily separated degradation products

2. Low volatility at lean conditions, preferably no volatility so that a water wash is unnecessary.
3. Commercially available in large quantities at low cost (less that \$10/lb)
4. Environmentally benign components and degradation products
5. Easily reclaimed from coal flue gas impurities such as sulfate, fly ash, metal, gypsum.
6. Compatible with inexpensive material of construction such as carbon steel and polymers.
7. Preferably two phase (gas and liquid). Additional liquid and solid phases can result in unreliable systems.
8. Non-foaming.

MEA is subject to oxidative and thermal degradation, [24, 25] but it is the least expensive amine and its losses are expected to be less than \$5/tCO_2. Impacts of SO_2, NO_X, and fly ash on solvent degradation will be minimized by efficient upstream equipment and a polishing scrubber. Oxidative degradation can be minimized by additives such as free radical scavengers [25]. Thermal degradation can be minimized by operating the stripping systems at lower temperature (e.g. 100 °C). Volatile amine emissions in the clean gas are easily avoided by a water wash section at the top of the absorber. Advanced amines such as proprietary hindered KS-1, piperazine [24], and ethyldiethanolamine [26] are resistant to degradation but are more expensive and will require more complex gas pre-treating to avoid economic losses from process upsets and the effects of SO_2, NO_x, and fly ash. More expensive solvents, such as ionic liquids, will be more economically sensitive to process upsets and other impurities, even if they are otherwise stable.

Recently, an innovative CO_2 capture system based on the formation of amidinium or guanidinium alkylcarbonate salts with good reactivity and high absorption capacity has shown interesting promise [27-31] This CO_2 capture system consists of an alcohol and a strong amidine (or guanidine) base. Compared with aqueous solution systems, the low specific heat and reduced hydrogen bonding in alkylcarbonate salts result in less energy intensive CO_2 release [32]. Unfortunately, volatilization of alcohol, as well as the recombination of CO_2 with volatilized species (i.e., alcohol and/or base) can lead to loss of organic solvent and increased operating costs associated with preventing CO_2 recombination losses during desorption. Hence, there remains a strong need to develop alternative technologies and approaches for the efficient and reversible capture of CO_2 without incurring loss of volatiles (e.g., alcohols, water).

3.1.3 Alternative Liquid Sorbents

Ionic liquids (ILs) are a class of compounds showing significant potential for CO_2 separation applications. Ionic liquids are organic salts molten below 100 °C whose cations, substituents, and anions can be varied virtually at will to tune their chemical and physical properties. Examples of typical cations and anions of ILs are shown in Figure 6. ILs act much like good organic solvents, dissolving both polar

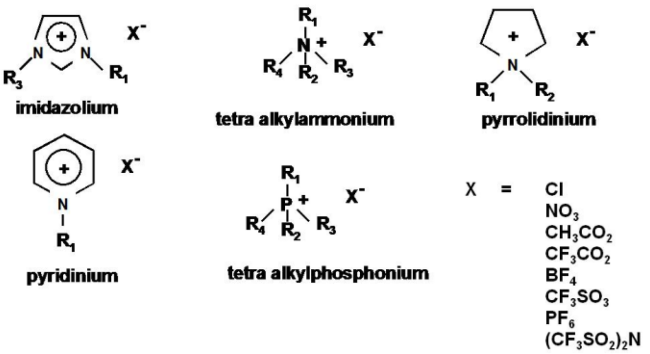


Figure 6. Examples of typical ILs [33].

and non-polar species. In many cases, they have been found to perform much better than commonly used solvents. Perhaps the most intriguing feature of these compounds is that, while they are liquid in their pure state at or near room temperature, they have essentially no vapor pressure. *They do not evaporate,* and so they cannot lead to fugitive emissions. Many of these compounds are liquids over incredibly large temperature ranges, from below ambient to well over 300 to 400 °C, which suggests they could be used under unique CO_2 processing conditions [33-35].

For use in CO_2 separations, the tunability of ILs is invaluable. There are virtually endless possibilities for cations, anions, substituents, and functional groups that can be incorporated into ILs. As a result, there are innumerable combinations possible, providing the opportunity to optimize physical and chemical properties for specific applications like CO_2 capture.

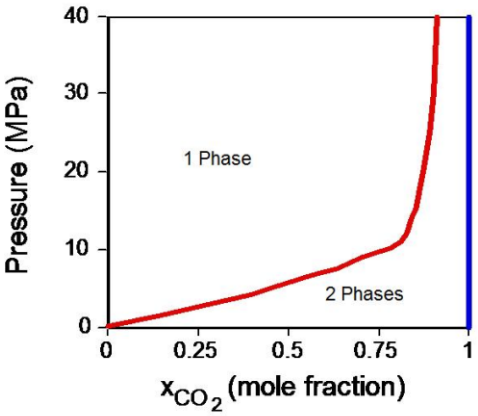


Figure 7. Phase diagram of CO_2 with 1-butyl-3-methylimidazolium hexafluorophosphate [36].

The solubility of CO_2 in an ionic liquid was first measured in 1999 [35], as shown in Figure 7. The discovery that CO_2 had significant solubility within ILs led to the idea of using ILs as a sorbent for separating CO_2 from other gases [37].

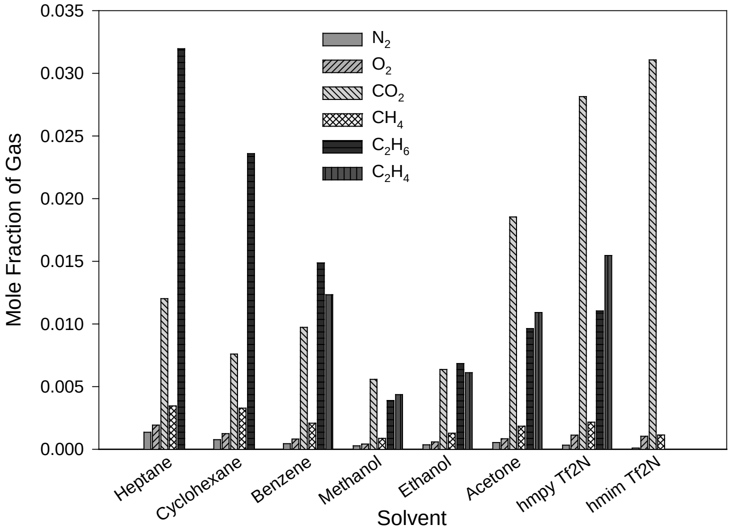


Figure 8. Solubility of CO_2 in various solvents at a partial pressure of 1 atm and temperature of 298.15 K [38].

The simplest way to separate CO_2 from other gases would be taking advantage of the difference in the physical solubility of the different gases in the ILs. Numerous investigations have shown the solubility of CO_2 in various different ILs increases with increasing pressure, reaching values as high as 20 or 30 mole % at 10 bar of partial pressure at 25 °C. As expected, CO_2 solubility decreases with increasing temperature. By comparison, the solubility of gases such as N_2 and O_2 in ILs tends to be quite low. This is shown clearly in Figure 8, where the solubility of various gases are shown at room temperature and 1 bar of partial pressure in common solvents and two ILs [37]. Clearly, the selectivity (solubility of CO_2/solubility of N_2 or O_2) is higher for the ILs than the common solvents.

3.1.4 Challenges and Technology Needs for ILs

Performing CO_2 separations using differences in physical solubilities in ILs would be best suited for applications where the CO_2 partial pressure is relatively high. An example would be separation of CO_2 from hydrogen or syngas produced from gasification of a fossil fuel or biomass (followed by reverse water gas shift).

The capacity of ILs for CO_2 using physical dissolution is too low for performing separation from post-combustion flue gas where the partial pressure of CO_2 is only 0.1 – 0.14 bar. In this case, ILs can be designed to have much greater affinity for CO_2 by incorporating functional groups that react with CO_2. Tethering an amine to the cation [39], first showed high capacity for CO_2, with chemistry similar to conventional amines, where two cation-tethered amines are required for each CO_2. Since the solubility of other gases, such as N_2 and O_2 is still low, this means excellent selectivity. Subsequently, it has shown that by tethering the amine to the anion, only one amine functionalized IL is required to complex one CO_2 molecule [40]. With 1:1 stoichiometry and since no added water is required, it is possible to achieve high CO_2 capacity, even on a volumetric basis, even though the IL is higher molecular weight than conventional amines. More importantly, by choice of the anion and cation, it is possible to tune the enthalpy of reaction. As a result, systems-modeling shows that it should be possible to achieve a 30% reduction in the parasitic energy requirements for the post-combustion CO_2 capture system using functionalized ILs compared to aqueous MEA [41]. One potential challenge with functionalized ILs is that there have been numerous reports that their viscosity increases substantially when they complex with CO_2 [42], rendering them unsuitable for a conventional absorber/stripper process system. This increase in viscosity also occurs with conventional amines; however, the dilution of conventional amines with water, which has a low viscosity of just 1 cP at ambient conditions, ameliorates this problem. Rather than diluting the ILs with a low viscosity solvent, one can solve this problem with appropriate tailoring of the chemistry [43]. Therefore, there are now functionalized ILs that react with CO_2 and have high CO_2 capacity but that do not increase in viscosity.

The potential benefits of IL sorbents over conventional aqueous amines include:

- extremely low volatility
- the opportunity to regenerate the IL sorbent over a wider range of temperatures in order to minimize parasitic energy loss
- elimination of the need to dissolve the sorbent in water
- less energy loss in the regeneration step to evaporation of water since the sorbent is not an aqueous solution
- potentially lower corrosion, in part due to the low water content
- significantly lower parasitic energy losses, as demonstrated by systems modeling
- the potential to even further tune the ILs for CO_2 capture applications by choice of anion, cation and functional groups

There are a number of challenges, providing opportunities for research, associated with the use of ILs for CO_2 capture applications.

1. Most importantly, these compounds are new and not available commercially in bulk quantities. In particular, functionalized ILs suitable for post-combustion CO_2 capture are still in the laboratory development stage. As a result, significant effort would be needed to produce commercial quantities at reasonable prices.
2. In addition, the functionalized ILs developed to date contain amine functionality so they would still be susceptible to poisoning by SO_2. Therefore, the use of ILs for post-combustion CO_2 capture would not eliminate the flue gas desulfurization step. By contrast, many non-functionalized ILs suitable for CO_2 separations by physical solubility differences are completely tolerant to SO_2. In fact, SO_2 is very soluble in them so simultaneous CO_2 and SO_2 removal might be possible. Other unknowns include tolerance to other impurities in pre- or post-combustion flue gas, long term stability and exact corrosion rates.
3. Finally, for functionalized ILs that react with CO_2, we lack any sort of fundamental molecular-level understanding of the reaction mechanism and the kinetics.

3.1.5 Ionic Liquid-Supported Membranes

Polymer-based membranes are being investigated as an alternative separation material because they are less energy intensive, undergo no phase change in the process, and typically provide low-maintenance operations. Polymer membranes have been used successfully in a number of industrial applications, including air separation. Recently published systems analysis and feasibility studies demonstrate that membranes are a technically and economically viable option for CO_2 capture from flue gas exhaust in coal fired power plants [44-46]. Membrane performance is dictated by the membrane permeance (pressure normalized flux) and selectivity for the components of interest. In the case of flue gas separation, the CO_2 permeance and the selectivity for CO_2 over N_2 are of primary interest. Commercially available membranes for CO_2 separation from air have low CO_2 permeance characteristics, ca. 100 GPU (1 GPU = 10^{-6} $cm^3cm^{-2}s^{-1}cmHg^{-1}$). All else equal, the membrane area required for a given application scales linearly with the permeance for a given gas flux through the membrane. Thus, a ten fold increase in permeance equates to a ten fold decrease in the membrane area required to achieve the same productivity. Reduced membrane area requirements also translate into smaller membrane footprint requirements and correspondingly better system economics. In a recent study, Merkel et al. have shown that the optimal membrane selectivity for separation of CO_2 from flue gas is in the range of 20 to 40 and that increasing membrane permeance is *the* critical factor to reduce capture costs [47]. For example, they show that for a given process scheme, a system comprised of a membrane with a selectivity in the aforementioned range and CO_2 permeance of 1000 GPU results in a cost per ton of CO_2 captured of ~$32 (Figure 9)

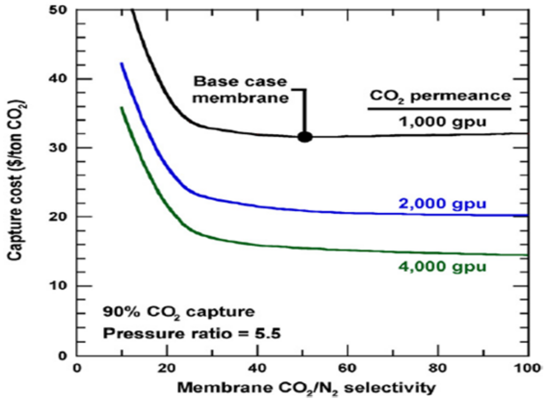


Figure 9. Effect of membrane CO_2/N_2 selectivity on the cost of capturing 90% of the CO_2 in flue gas for membranes with a CO_2 permeance of 1000, 2000, and 4000 gpu at a fixed pressure ratio of 5.5 [47].

A 4-fold increase in CO_2 permeance to 4000 GPU decreases this cost by nearly 50% to ~$18. While the reduction of separation cost versus gas permeance is nonlinear, it is clear that a permeance of 10,000 GPU would result in a cost per ton of CO_2 captured of less than $10. This is a ***significant*** reduction compared to both the benchmark amine technology and the current membranes under development for this application. Realization of such a high permeance membrane would be a transformational achievement resulting in a membrane based separation technology for post combustion CO_2 capture that would ***exceed*** the current DOE targets ($20-25 per ton of CO_2; <35 % increase in COE) in sensational fashion. Production of a membrane with a selectivity of at least 20 and a permeance of at least 10,000 GPU is the goal. One way achieve this goal these high permeances and selectivity is a combination of ILs and membranes.

3.1.6 Challenges and Technology Needs for ILs and Polymer Membranes

Unlike traditional organic media, the properties of ILs may be adjusted via chemical alteration of the cation or anion to produce application specific compounds. Thus, the potential exists to tune the IL such that one of the ions (cation or anion) functions as a complexing agent for the desired sorbate, tremendously increasing the sorption capacity of the IL. Recent studies on ILs indicate that the combination of subtle (*e.g.*, changing cation substitution patterns) and gross (*e.g.*, changing the anion type) modifications enables very precise tuning of the IL solvent properties [48]. Changes in solvation properties are possible in this way, thus enabling the rational design of application specific ILs. These so-called “task specific” ILs can also be “tuned” to absorb very high quantities of a specific gas, e.g. CO_2. For example, Davis and co-workers reported the synthesis of an IL containing an amine functionality that was capable of absorbing 0.5 mol of carbon dioxide per mole of IL (approx. 6 mL/g IL) [39].

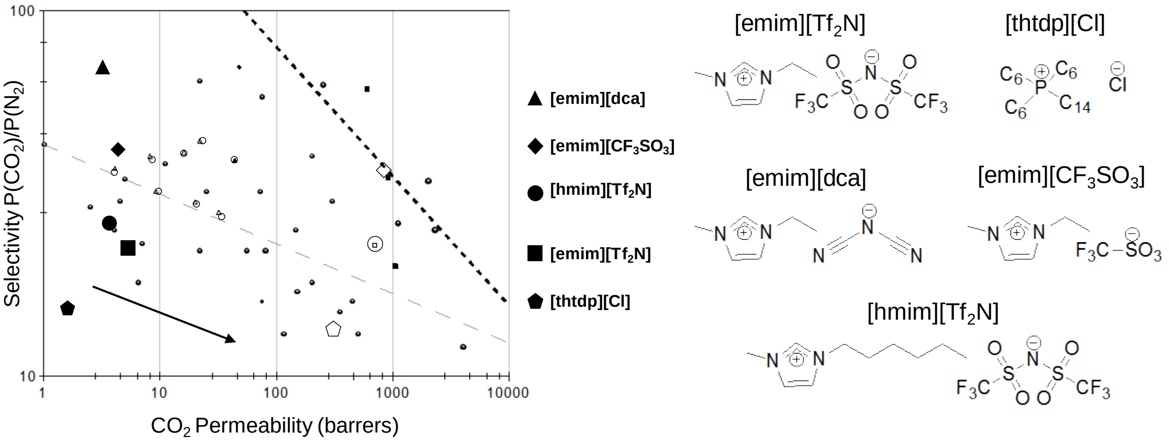


Figure 10. (Left) Robeson plot of ionic liquids used as SLMs and representative polymers (small circles) [52]. (Right) plot of selectivity vs. permeability for CO_2/N_2 separations. Ionic liquids exceed the “upper bound” observed for polymer membranes.

Previous research has demonstrated that supported liquid membranes (SLMs) containing ILs can be prepared and used for gas separations [39, 49, 50]. We have demonstrated that relatively stable SLMs could be made by impregnating commercially available micro-porous hydrophilic polymeric (polyethersulfone (PES)) or ceramic (Alumina Anodisc®) substrates. These membranes exhibited a combination of high permeability [51] and selectivity for carbon dioxide as shown in Table 4 and Figure 10 [49]. Further, Condemarin et. al. recently reported exceptional long term stability of SILMs in mixed gas testing [53]. All these data demonstrate the significant potential of IL-SLMs for CO_2 capture from flue gas.

The ability of materials to perform a particular separation in a membrane format is frequently represented on Robeson plots of selectivity vs. permeability [54]. For the separation of CO_2 and N_2, several emim-containing ILs have demonstrated performance well above that represented by the so-called Robeson upper-bound observed for dense polymers, *including commercial ones* (Figure 10, Table 4). They also have demonstrated excellent stability in chemically challenging environments as well as thermal stability over a broad temperature range (sub-ambient to > 200 ° C). As a result, this class of materials has separation performance characteristics that demonstrate their potential as a medium for the removal of CO_2 from flue gas. The industrial implementation of this class of exciting materials has not yet been realized for this application due to low productivity (permeance) and the mechanical stability limitations inherent to the IL-SLM format.

Table 4. Gas transport properties of various supported ionic liquid membranes. Some unpublished data recently obtained by the Noble group is also included [55] (PES: polyethersulfone; PSF: polysulfone).

Ionic Liquid	**Support**	**CO_2 Permeability (Barrer)**	**CO_2/N_2 selectivity**	**Reference**
[emim][Tf_2N]	PES	960	21	Scovazzo[53]
[emim][CF_3SO_3]	PES	920	35	Scovazzo[53]
[emim][dca]	PES	610	61	Scovazzo[53]
[thtdp][Cl]	PES	350	15	Scovazzo[53]
[$H_2NC_3H_6$mim][Tf_2N]	nylon	80	-	Myers[56]
[hmim][Tf_2N]	PSF	860	-	Llconich[57]
[bmim][BF_4]	PES	2500	55	Zhao[58]
[C_6mim][Tf_2N]	PES	700	23	Voss[50]
[C_6mim][Tf_2N]	PES	650	22	Voss[50]
[emim][Tf_2N]	Anodisc	1628	36	Noble[55]
[emim][dca]	Anodisc	946	58	Noble[55]

Thus, the key challenges hindering the realization of a transformational separations technology based on IL membranes for flue gas application are:

1. The achievement of a mechanically stable, commercially viable IL membrane platform that retains the chemical stability, thermal stability, and permselectivity characteristics that have been demonstrated in this class of materials.
2. Realization of such a platform in concert with the development of a fabrication/coating technology to enable preparation of very thin, high permeance, defect-free selective layer films (≤ 1 µm) on a suitable support. The ultimate game changing technology resulting from the successful achievement of those goals would be a chemically, mechanically, and thermally robust IL-based membrane system with a permeance of > 10,000 GPU and a selectivity of at least 20 under industrially relevant operating conditions (see Figure 9) that will ***exceed*** the current DOE targets ($20-25 per ton of CO_2; <35 % increase in COE) in sensational fashion.
3. A commercial process for removal of smoke and oxides of sulphur from flue gases

3.2 Solid Adsorbents

New classes of solid adsorbents are being investigated to complement the existing arsenal of ionic liquid absorbents and transport-controlling membranes. These new hybrid materials consist of metal ions with well-defined coordination geometry linked to organic bridging ligands.

3.2.1 Metal-Organic Frameworks (MOFs)

Over the past decade, metal-organic frameworks (MOFs) have emerged as a new class of microporous solids exhibiting record surface areas of up to 5200 m^2/g, as well as tunable pore sizes and surface chemistry [59]. MOFs, also known under the names such as porous coordination polymers, are typically crystalline powders obtained from a high-dielectric solvent by reaction of a metal salt with a multitopic organic bridging ligand capable of linking the metal cations into a porous three-dimensional network structure. Subsequent heating under dynamic vacuum or treatment by supercritical drying [60] evacuates the solvent molecules from the pores of the structure without destroying the network connectivity and crystallinity. Owing to their exceptionally high surface areas, these materials can exhibit tremendous capacities for compressed gas storage, delivering the highest known storage densities for CH_4, C_2H_2, CO_2, and cryogenic H_2 [61]. A high surface area is also beneficial for CO_2 capture, where it can ensure a high loading capacity and, assuming good permeability, rapid adsorption as a result of the large gas-solid interface. Most importantly, however, MOFs offer the possibility of using the power of synthetic chemistry to tailor the nature of their internal surfaces and thereby adjust the CO_2 adsorption selectivity.

MOFs are of potential utility for capturing CO_2 under a variety of scenarios. Of particular interest is capture from the flue gas emitted by fossil fuel power plants using a pressure and/or temperature swing adsorption process. They are additionally of interest for applications in natural gas sweetening, in the efficient capture of O_2 from air for oxyfuel combustion, and in precombustion capture of CO_2 from the higher pressure (50-60 bar) synthesis gas obtained upon coal gasification. For this last application, further research into methods for integrating MOFs within membranes is essential. Finally, it should be noted that MOFs are also of possible value for the transport of compressed CO_2 gas subsequent to capture [61c].

For adsorptive separations, differences in size and/or electronic properties can be utilized. The major separation issue for a flue gas with an overall pressure of 1 bar is the separation of CO_2 (ca. 15-16 % by weight) from N_2 (70-75%), ideally in the presence of water vapor (5-7%) and O_2 (3-4%). Separations can be achieved on the basis of the smaller kinetic diameter of CO_2 (3.30 Å) compared with N_2 (3.64 Å), but it should be kept in mind that the small pore sizes required may severely impede gas permeation. Typically, CO_2 is preferentially adsorbed over N_2 because it has a greater polarizability (29.1×10^{-40} cm^3 vs. 17.6×10^{-25} cm^3) and quadrupole moment (-13.4×10^{-40} Cm^2 vs. -4.7×10^{-25} Cm^2). For a high selectivity to be achieved, the adsorbent should have a large heat of adsorption for CO_2 compared with the other gases; however, increases in selectivity will also come with a penalty in the energy required to release the CO_2 and regenerate the adsorbent.

Structural Considerations: The following are some structural issues worthy of consideration in attempting to design MOFS suitable for CO_2 capture from flue gas.

Surface area. As mentioned, the very high surface areas of MOFs can be an advantage for achieving a high gravimetric CO_2 adsorption capacity. Surface areas in excess of 4000 m^2/g have been reported for a number of MOFs [62]. When making comparisons of surface areas, however, one must be careful to ensure that the values have been calculated correctly [63]. Of course, it is also important that the exposed surface area within a MOF have a strong affinity for CO_2 if a high loading capacity is to be achieved at the relevant partial pressure of 0.1 bar.

Pore size. MOFs featuring small pore openings can serve to give selectivity for CO_2 over N_2 by restricting access to the larger N_2 molecules. For example, $Mn(HCO_2)_2$ with 4.5-Å zig-zag channels exhibits a 10-fold selectivity for adsorbing CO_2 over N_2 or CH_4 at 1 bar and 195 K [64] To obtain narrow pores, one can utilize short bridging ligands, such as formate in this example, or rely upon interpenetration, wherein two or more distinct networks are interwoven. Another means of using pore size for gaining selectivity is by taking advantage of the temperature-dependent dynamics of substituents on the bridging organic ligand (e.g., *t*-butyl groups) positioned near the pore openings [65] In all of these cases, it will be important to measure the kinetics of flue gas permeation. Indeed, it is not yet clear, but it may in fact prove necessary to have quite large pore openings (of ca. 10 Å diameter or greater) to ensure rapid permeance of the flue gas.

Framework flexibility. Certain MOFs can exhibit a structural flexibility in which the framework retains connectivity while undergoing a breathing motion, typically involving a volume change of 50-85%, in response to a gas or liquid [66]. For example, Cr(OH)(BDC) (MIL-53(Cr)) flexes upon interaction with CO_2, resulting in a contraction of the framework at pressures of 1-4 bar. On increasing the pressure of CO_2 to ca. 6 bar, the structure expands and the pores widen to adsorb more CO_2 [67]. Since no equivalent effect occurs for CH_4, a comparison of single-gas isotherms suggests a very high selectivity for CO_2 over CH_4. The results of breakthrough experiments performed with CO_2/CH_4 mixtures at 10 bar and 303 K show that selectivity is indeed observed in the mixed gas system, although it is not as high as predicted from the single-gas isotherms [68]. In general, it is not clear if this mechanism is truly viable for performing gas separations, since once one of the gas components triggers pore opening, all of the gases may then be permitted entry.

Affinity of the Surface for CO_2. Given the low partial pressure of CO_2 in a flue gas (ca. 0.1 bar), it is essential that the internal MOF surface have a high selectivity for binding CO_2 preferentially over N_2. At least two methods for accomplishing this are now well-established.

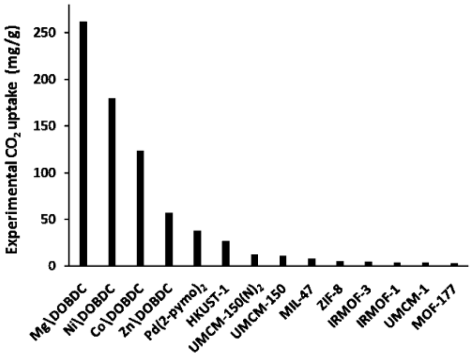


Figure 11. Comparison of CO_2 uptake capacities for selected MOFs at 0.1 bar and 293-298 K [70]. Note that DOBDC = dhtp.

Exposed metal cation sites. Owing to the greater polarizability and quadrupole moment of CO_2, variations in the charge distribution on the MOF surface can provide an excellent means of achieving selectivity over N_2. In particular, the large positive charges created upon desolvation and exposure of a metal cation embedded within the surface can afford a strong induced dipole interaction with CO_2. A range of MOFs of this type have been created and evaluated for hydrogen storage applications, [69] and many of the same materials are of potential interest for CO_2 capture. Of the examples tested to date (see Figure 11), [70] the most promising by far are the isostructural compounds M_2(dhtp) (M = Mg, Co, Ni, Zn; H_2dhtp^{2-} = 2,5-dihydroxyterephthalate). [71] These MOFs contain one-dimensional hexagonal channels that are lined with a high concentration of exposed M^{2+} cations, each capable of binding a CO_2 molecule in an end-on fashion (see Figure 12). [71b] Within this series, Mg_2(dhtp) exhibits the best performance in terms of uptake capacity (23.6 wt % or 5 mmol/g of CO_2 at 0.1 bar and 296 K) and the heat of CO_2 adsorption (–47 kJ/mol). This MOF has also been utilized in the quantitative separation of CO_2 over CH_4 in breakthrough experiments, where it was further shown that after loading the CO_2 can be readily removed by heating at 80 °C [71c]. The ability to obtain an isostructural family of compounds with different metal cations is potentially important here, since variation of the charge density at the exposed metal site provides a powerful means of adjusting the CO_2 adsorption enthalpy to match with that needed for a specific power plant design.

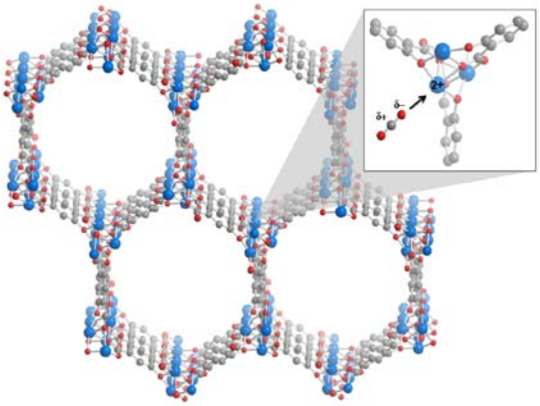


Figure 12. A portion of the crystal structure adopted by the MOFs M_2(dhtp) (M = Mg, Co, Ni, Zn), wherein open M^{2+} cation sites lead to a preferential binding of CO_2 over N_2.

Surface functional groups. Coating MOF surfaces with polar functional groups can provide another means of gaining selectivity for CO_2 adsorption. In particular, substituents on the organic bridging ligands, including chloro (-Cl), bromo (-Br), fluoro (-F), nitrile (-CN), nitro (-NO_2), and amino (-NR_2) groups can enhance the electronic interaction with CO_2. Amine groups are perhaps most noteworthy here, since aqueous solutions of ethanolamine are currently used commercially for CO_2 scrubbing. In general, alkylamine groups will react reversibly with CO_2 to form either carbamates via nucleophilic attack of the lone pair of the amino group on the C atom of CO_2, or ammonium bicarbonate. By functionalizing a MOF surface with dangling alkylamine groups it should therefore be possible to create a solid adsorbent with a very high CO_2 binding selectivity. Importantly, it should be possible to adjust the strength of the interaction with CO_2 by varying the R groups of the amine. Indeed, aromatic amino groups are much less basic, and accordingly have a relatively weak interaction with CO_2.

Modeling CO_2 Adsorption and Transport in MOFs: Molecular-level modeling is playing an important role in improving our understanding of CO_2 adsorption and transport in MOFs. Molecular simulations based on classical mechanics and statistical mechanics can predict uptake amounts of CO_2 and other small gases in MOFs, heats of adsorption, selectivity for mixtures, diffusion coefficients, and detailed molecular-level information on where molecules sit within the MOF pores and how they move. Quantum mechanical (QM) calculations can provide information on binding of CO_2 to strong adsorption sites, as well as energetic and other information that can be fed into Monte Carlo simulations, but the QM methods do not directly predict adsorption isotherms. The application of these methods to adsorption and diffusion in MOFs has recently been reviewed [72].

Initial work in the field focused on modeling one material at a time, testing the ability of simulations to predict adsorption isotherms in agreement with experiment, and using simulation results to obtain additional insights beyond those available from experiment. Currently, there is a shift to screening larger numbers of materials. Figure 13 shows that simulated isotherms for CO_2 in MOF-177, IRMOF-1, and IRMOF-3 are in excellent agreement with experimental data [73]. It should be noted that the simulation results were not fit in any way to this data; nevertheless, they are able to capture the complex shapes of these isotherms essentially quantitatively. The CO_2 isotherm in IRMOF-1 shows an unusual inflection at 298 K, which grows into a distinct step as temperature is decreased. Further analysis of the results shed additional light on the cause of the inflection and steps and showed that the pore-filling pressure shifts toward the bulk condensation pressure with increasing pore size [73].

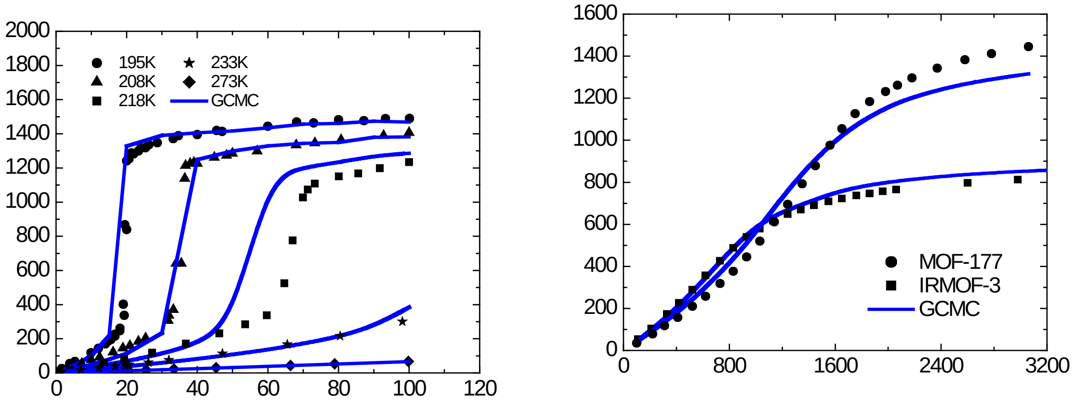


Figure 13. Left: Comparison of adsorption isotherms for CO_2 in IRMOF-1 at various temperatures from grand canonical Monte Carlo (GCMC) simulations (lines) and experiments (symbols). Right: Comparison of adsorption isotherms for CO_2 in MOF-177 and IRMOF-3 at 298 K from GCMC simulations and experiments.
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Researchers have recently begun to compare CO_2 uptake across families of different MOFs. For example, Yang et al. [74] investigated the effects of organic linker, pore size, pore topology, and electrostatic fields on the adsorption of CO_2 in nine different MOFs. They found that the enthalpy of adsorption plays an important role at low pressures, so that there is a correlation between CO_2 uptake and the adsorption enthalpy. At higher pressures, CO_2 uptake correlates with the material surface area and free volume. A similar trend was observed by Yazaydin et al. [70], who examined a more diverse group of 14 MOFs and reported experimental uptake at conditions relevant for flue gas capture in addition to results from molecular simulation. The simulation results were in good agreement with experiment, especially in ranking the MOFs for CO_2 uptake at 0.1 bar (representative of flue gas conditions). For example, the simulations correctly predicted the top 5 MOFs for uptake of CO_2 at 0.1 bar in agreement with experiment [70]. It should be emphasized that good agreement between simulation and experiment relies on careful characterization of the materials used in the experiments. Simulations model adsorption in the "perfect" MOF crystal structures reported from single-crystal x-ray diffraction. If powder samples used for adsorption measurements differ from these structures, one should not expect good agreement between simulation and experiment. Deviations could include partial collapse of the MOF upon solvent removal, residual solvent molecules in the MOF pores, or unreacted molecules from the MOF synthesis.

3.2.2 Zeolitic Imidazolate Frameworks (ZIFs)

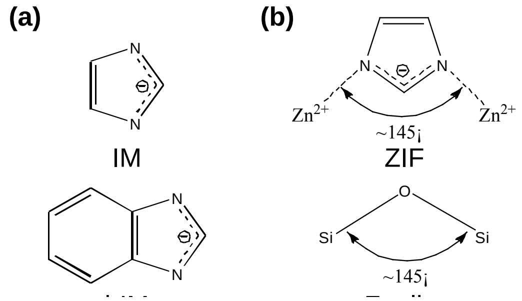

Figure 14. (a) Structure of an imidazolate anion [top], and a benzyl-substituted imidazolate [bottom]. (b) Comparison of ZIF and zeolite structures, showing a similar bond angle; adapted from Ref. 59.

Zeolitic imidazolate frameworks (ZIFs) are a subclass of metal-organic frameworks that consist of a tetrahedral cation coordinated by an organic imidazolate (IM) bidentate ligand, or substituted derivative thereof [75]. In the large majority of ZIFs that have been synthesized to date the central cation is Zn^{2+}, although several examples of ZIFs containing Co^{2+} can be found in the literature [75-77]. ZIFs carry their "zeolitic" moniker not from any *chemical* similarity to silicon-based zeolites, but rather due to their *structural* analogy: the Zn-IM-Zn bond angle in a ZIF is nearly identical to the Si-O-Si in conventional zeolites (Figure 14) [75]. This correspondence leads to the formation of similar three-dimensional structures for both compounds, containing large pore regions, interconnected by (typically) more constricted entrances (apertures) (Figure 15). Yet in contrast to traditional zeolites, ZIFs offer tremendous potential for design and modification, allowing for control of the physical (pore size, aperture diameter) and chemical properties by functionalization of the organic IM linker [78]. This flexibility opens entirely new possibilities that are inaccessible using traditional zeolite chemistry.

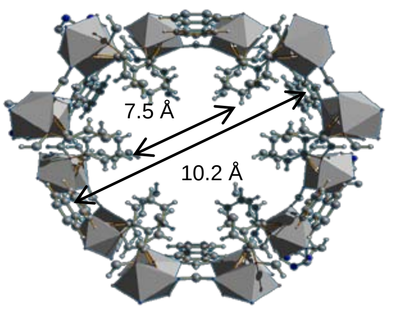

Figure 15. ZIF-68, with a large cavity and smaller aperture. Aperture sizes range from 0.7–13Å in various ZIFs.

Like the MOFs counterparts, ZIFs form stable, three-dimensional, crystalline microporous solids. Due to their porous nature and large interior pores, ZIFs possess very low density, and extraordinarily high surface areas, often in excess of 1000-2000 m^2/g [77, 78]. Furthermore, recent studies indicated that ZIFs may display very good selectivity for CO_2 [77-80]. Both the capacity and selectivity of the ZIFs can be influenced and tailored by proper functionalization of the IM linker [77, 78]. This was recently demonstrated in an isostructural series of ZIFs of formulae Zn(nIm)(Lbim) (nIm^- = 2-nitroimidazolate; $Lbim^-$ = 5-L-benzimidazolate where L is a variety of functional groups) [[80]. Thus, at 1 bar and 298 K, the CO_2 uptake selectivity was found to vary along the series: L = NO_2 (ZIF-78) > CN, Br, Cl (ZIF-82, -81, -

69) > C_6H_6, Me (ZIF-68, -79) > H (ZIF-70) > BPL carbon (Figure 16). Most notably, the uptake capacity for the nitro-functionalized structure (ZIF-78) is nearly three times that of commercial BPL carbon, with more than twice the selectivity over N_2.

While selective adsorption serves as one mechanism for potential gas separation, the unique structure of ZIFs, containing large pores with small apertures, provides an additional pathway for gas separation: kinetic separation [81, 82]. The controllable aperture diameter of ZIFs means that it may be possible to design a ZIF with an aperture sized to allow the passage of one gas, while excluding (partially) the flux of a second gas.

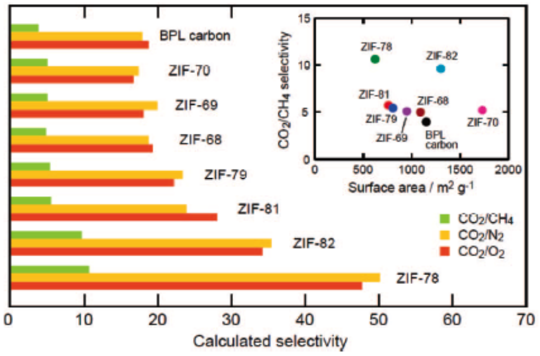

Figure 16. Selectivity for CO_2 binding over CH_4, N_2, and O_2 in selected ZIFs adopting the *gme* structure type and having a variety of surface functional groups.

The performance of ZIFs as selective adsorbents for carbon dioxide ultimately depends on their specific interactions with the CO_2 molecules. Although little direct experiment data (such as neutron or x-ray diffraction) exists to date, molecular simulations yielded some insight about the predominant interaction mechanisms [82, 84]. These simulations employ empirical interaction potentials, and the results depend somewhat sensitively on the exact force field employed. In such simulations, the most favorable adsorption site for the CO_2 is found to be in the small cages of the ZIF [84]. At low pressures the predominant interaction is between CO_2 and the polar substituents of IM, localizing in the small pores made by the polar groups [83]. The electrostatic interactions of the CO_2 with the framework atoms is quite significant, and cannot be neglected at or below ambient pressures; at much higher pressure (above those likely applicable for flue gas separation) the effect of electrostatic interaction seems to become of secondary importance [85].

ZIFs exhibit impressive thermal stability [75], up to 500 °C, which is moderately higher than for prototypical MOFs [77, 78]. Yet it is the chemical and solvent stability of ZIFs that strongly differentiates them from most other MOFs, displaying excellent resistance to many common solvents [75]. For example, a group of ZIFs were shown to be resistant to 7 days of refluxing in both benzene and methanol [77, 80]. Another ZIF, ZIF-8, was resistant to 7 days of exposure to 50 °C water, and even to 24 hours in 0.8M NaOH at 100 °C [75]. The enhanced chemical stability of ZIFs facilitates their post-synthetic functionalization, allowing for modulation of the CO_2 capacity and selectivity [86]. The unusual solvent resistance of ZIFs has been attributed to either unusually strong metal-ligand bonds, or the hydrophobic nature of the ZIF ligands protecting the sensitive metal-ligand bonds to hydrolysis [75]. Some support for the latter hypothesis is given by subsequent experimental work on water adsorption, where it was shown that ZIF-8 is extremely hydrophobic [87]. In fact, the ZIF displays almost no water adsorption until the condensation point is reached. Note that in this work, in contrast to that of Park et al., this later work found a few additional peaks in the powder XRD spectrum after exposure to water at 50 °C for 24 hours, suggesting that although their solvent resistance is good, the ZIFs are far from inert [87].

3.2.3 Current Limitations in CO_2 Capture by MOFs and ZIFS

It seems clear that it will be feasible to develop MOFs with truly outstanding levels of performance in the separation of CO_2 from mixtures with N_2. Their eventual use on the enormous scale required for CO_2 capture from power plant flue gases, however, still presents a number of serious challenges. Some of the issues to consider are economical, with uncertainties arising, for example, in the availability of materials and the ultimate costs of manufacture of MOFs if they are to be produced on such an enormous scale. Other challenges involve fundamental science. For example, little is currently known about the necessary physical and chemical properties of the sorbent that would be required for utilization in a practical flue gas separation system. While these properties would depend on the detailed structure of the separation system, even order of magnitude estimates would be extremely useful. In particular, estimates for the for the following are required: capacities (translated into laboratory measurable units, such as mmol CO_2 / g or mmol CO_2 / L of sorbent at a given pressure or temperature), adsorption selectivity for CO_2 over other relevant flue gases, transport diffusion constants for CO_2 through the sorbent, and heat of CO_2 adsorption, are essential for guiding future synthetic work.

Our fundamental understanding of the interaction of MOFs and ZIFs with CO_2 and other flue gases, in particular N_2 is still limited. Experimental efforts to probe these interactions via either diffraction studies or spectroscopic (IR, perhaps even NMR) methods may provide valuable insight that is not currently available. Additional insights can also be gained through computational techniques, including molecular simulations and electronic structure methods. These computational efforts are somewhat hindered by the fact that different empirical force fields have yielded different results, and the weak intermolecular interactions between the framework and adsorbate are difficult to probe using common density functional theory techniques. On the other hand, it remains particularly difficult to predict the CO_2 uptake in MOFs that contain open metal sites or other strongly interacting functional groups. The models typically used in current simulations are based on a classical "force field" model and do not take into account orbital interactions and thus are generally not expected to perform well for strong binding sites.

In addition to the above-mentioned fundamental problems, there are some practical issues that need to be resolved before MOFs and ZIFs can be used effectively for CO_2 capture:

Performance in the Presence of Water. The management of water will be an important factor for the industrial application of MOFs in CO_2 capture. Unless rigorously dried, most industrial gas streams contain some amount of moisture, and untreated flue gas contains 5-7% water vapor by weight. Ideally, a MOF suitable for CO_2 capture should be stable to the sustained presence of water vapor at this level. Although many MOFs are unstable to water, a growing number are held together by very strong metal-ligand bonds and can survive even extreme hydrothermal conditions [87]. Importantly, the MOFs displaying a high water stability include Mg_2(dhtp), $HCu[(Cu_4Cl)_3(BTTri)_8]$, and most ZIFs [71, 80, 89]. In addition, since water has a large dipole moment, it will tend to adsorb to charged sites on a MOF surface preferentially over CO_2, potentially interfering with CO_2 capture. In general, many more measurements on MOFs using mixed gas streams that include water vapor are needed to probe what effects water will have. Interestingly, however, there are indications that certain MOFs may actually perform better in the presence of water [89].

Stability Towards Impurities. In natural, synthesis, and especially flue gas streams, there are impurities that can be acidic, such as SO_2, H_2S, HCl, and NO_x, and could potentially be corrosive to MOFs. Ideally, a MOF would be stable to exposure to any potential flue gas impurities; although certain of these gases may already be removed in power plants due to environmental legislations. Further measurements on the impact of such trace gases on MOFs are needed.

Gas Diffusion Rates. Most of the work on MOFs to date has focused on thermodynamic aspects of their performance. Equally important, however, is the kinetics of how a flue gas will permeate a MOF. Very few measurements of this type have yet been carried out, and many more are needed. Similarly, very little experimental or theoretical data exists for diffusion of CO_2 in ZIFs. Wang et al. noted that slow diffusion seems present during gas absorption (although this is not quantified), which they attribute to the effect of constricted pore apertures [79]. A handful of simulation studies have looked at diffusion in ZIFs and found that it could be up to an order of magnitude slower than in typical MOF systems [83, 84]. The decreased diffusion was attributed to the the smaller pores in the ZIF system, as well as steric hindrance due to substituents on the IM linkers. It would seem that experimental measurements of gas diffusion in ZIF systems are crucially important in order to evaluate whether the observed diffusion rates are sufficient for practical applications, or whether the ZIFs can be altered in a way to increase the diffusion rates without sacrificing gas adsorption capacity or selectivity.

Scalability. It is not yet clear whether the existing solvo-thermal synthetic procedures, used in both MOF and ZIF synthesis, can be applied to the extremely large scales that would be required for use in a flue gas separation system. Although this pathway has so far been scaled to the gram scale, it is likely that additional research would be required to achieve kilogram scale, and beyond.

Reversibility and Regeneration. Any flue gas separation system based on gas adsorption will need to be operated in a cyclic manner, using some mechanism (typically temperature or pressure swing) to regenerate the adsorption medium and release the adsorbate. While CO_2 adsorption in MOFs and ZIFs seems to be essentially completely reversible based on pressure swing, it is not yet clear whether the adsorption/desorption can be done over thousands of cycles without deterioration of performance. Ultimately this depends on the long-term stability of the frameworks, which need to be tested under conditions relevant to flue gas separations.

3.3 Membranes

Gas separation by membranes is highly desirable since separation by membranes is generally a low energy process. The selectivity of membranes can lead to highly pure streams and membrane based automated plants can remain in operation without requiring major maintenance. The CO_2 separation by membranes has been accomplished and is applied in natural gas processing industry. This section summarizes the status of gas separation membranes.

3.3.1 Types of Membranes

Both polymeric and inorganic membranes have been studied for gas separation. Inorganic membrane materials generally offer higher permeability and selectivity and better chemical and thermal stability than the polymeric membrane materials. However, polymeric materials can be more easily processed to thin, flexible membranes and to the modules with packing density. Polymer membranes are less expansive than inorganic membranes on the square footage basis. Although many polymer membranes have been investigated, only a limited number of polymer membranes are used industrially for gas separations [91]. These include rubbery polymers of poly (dimethylsiloxane), ethylene oxide/propylene oxide-amide copolymer, and glass polymers of cellulose acetate, polyperfluorodioxides, polycarbonates, polyimides, and polysulfone. Inorganic membranes studied for gas separation include amorphous and crystalline microporous silica, carbon and other ceramic membranes, metal membranes and crystalline metal oxide membranes [92]. Metal membranes are used in hydrogen purification in the semi-conductor industry and porous inorganic membranes have been used for large scale gas diffusion separation of uranium isotopes. There is currently a major industrial effort to develop crystalline ionic transport inorganic membranes for air separation and syngas production.

Membranes have potential for use in the post-combustion, pre-combustion and oxy fuel combustion processes for CO_2 capture. Oxygen semi-permeable mixed-conducting metal oxide ceramic membranes operated at temperatures above 700 ^{o}C are suitable for oxygen separation from air for oxyfuel combustion applications. Both H_2 and CO_2 selective membranes are considered for pre-combustion applications. The H_2 or CO_2 selective membranes operated at the high temperatures (above 700 ^{o}C) may be used in the membrane reactors for reforming reactions, and those in the temperature range of 300-500 ^{o}C are more suitable for use in the membrane reactors for water gas shift reaction, a key step in the pre-combustion process. Low temperature CO_2 selective membranes have also been considered for pre-combustion CO_2 capture but in principle the combined membrane separator/reactor process is not as efficient as the high temperature membrane reactor. Therefore thermally stable inorganic membranes are most suitable for pre-combustion and oxyfuel combustion CO_2 capture applications.

For post-combustion CO_2 capture, the membrane should be operated in the temperature range of 50-150°C, the temperature of flue gas leaving the flue gas desulfurizer (typically a wet-lime scrubber). This temperature range fits the operation conditions of both polymer and inorganic membranes. The flue gas contains roughly about 15% CO_2, 5% O_2, 70% N_2, 10% H_2O, and other impurities (see Fig. 2, Section 2). For post-combustion CO_2 capture, the membrane is used primarily to separate CO_2 from N_2. So CO_2 permeance, CO_2/N_2 permselectivity, chemical and mechanical stability, material processibility and membrane costs are the main considerations for selecting a membrane for post-combustion CO_2 capture.

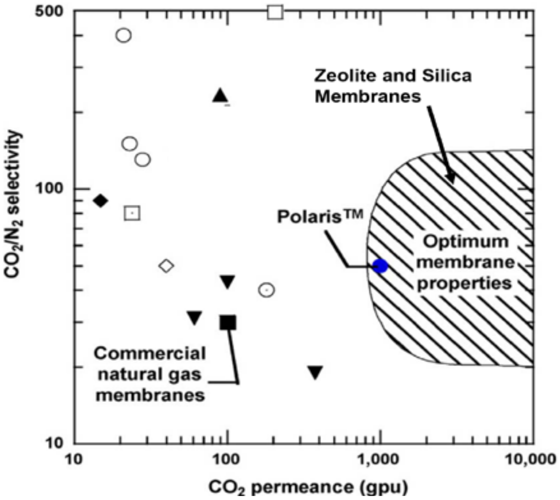

Figure 17. Comparison of CO_2/N_2 selectivity and CO_2 permeance of various polymer and composite membranes (points) with those of commercial membranes for acid gas removal from natural gas (full square), Polaris membrane (full circle), and microporous inorganic membranes (modified from [95]).

Polymeric Membranes: A large number of polymer membranes have been studied for CO_2/N_2 separation including polyacetylenes, polyarylene ethers, polyarylates, polycarbonates, polyimides, polyprrolones and polysulfones [93, 94]. Most polymer membranes have CO_2/N_2 selectivity in the range from 5 to 50 and CO_2 permeability up to about 600 Barrer (2.0x10^{-12} mol/m·s·Pa) [95]. Many polymer membranes suffer from a chemical stability problem; in particular, CO_2 induced plastization [92]. The polyimide membranes appear most attractive for CO_2 capture due to their good physical properties and structural variability, ease of membrane formation, and desired gas transport properties. Polymer membranes with higher CO_2/N_2 selectivity have been reported, but mostly achieved through the mechanism of facilitated transport of CO_2. Recently Membrane Technology and Research Inc. (MTR) has reported a rubbery polymer membrane called "Polaris" (detailed composition and material not revealed [95]). The membrane exhibits a moderate CO_2/N_2 selectivity (about 50) but high CO_2 permeance (1000 GPU, or 3.3x10^{-7} mol/m^2·s·Pa) [95]. Figure 17 compares selectivity and permeance of the Polaris membrane with other representative polymer or composite membranes for CO_2 capture, along with the desired range for membranes properties obtained by simulation of membrane separation process [95].

Inorganic Membranes: Inorganic membrane materials are known for their better chemical and thermal stability and higher perm-selectivity for gas separation than polymer membranes. The majority of inorganic membranes studied for CO_2 separation are microporous membranes including zeolite membranes, sol-gel derived or chemical vapor deposited silica or zirconia membranes, carbon membranes, organic modified silica membranes, and inorganic-polymer composite membranes such as mixed-matrix membranes. CO_2 and N_2 have a kinetic diameter respectively of 0.33 and 0.36 nm, very close to each other. However, the quadrupole moment for CO_2 is about 3 times larger than that for N_2 [96]. Thus, many inorganic membranes are perm-selective for CO_2 over N_2 due to preferential adsorption of CO_2 on the membrane material and, to much less extent, the smaller molecular size of CO_2 as compared to N_2. Sol-gel derived silica membranes and NaY and KY zeolite membranes show CO_2/N_2 selectivity up to 70-100 with CO_2 permeance in the range of 1-5x10^{-7}mol/m^2·s·Pa at room temperature. These microporous inorganic membranes already have CO_2/N_2 selectivity and CO_2 permeance in the desired range shown in

Figure 17. However, these microporous inorganic membranes become essentially non perm-selective for CO_2/N_2 separation at high temperatures (>300 °C).

Gas/vapor permeation through microporous inorganic membranes is determined by adsorption and diffusion of the permeating species in the membrane pores [92]. At low temperatures the CO_2/N_2 perm-selectivity for these microporous inorganic membranes is mainly determined by the adsorption properties of the membranes for CO_2 and N_2. Their pore sizes are still too large to show any significant diffusion-controlled selectivity for CO_2 over N_2 [97, 98]. For MFI or FAU type zeolite membranes, with zeolite pore diameter respectively of 0.55 nm and 0.7 nm, the ratio of the molecular size to pore size, λ, is smaller than 0.75 for CO_2 and N_2. If one considers possible microporous defects, the average pore size of the membranes would be even larger than the zeolite pores, yielding a much lower value of λ. With λ in this range, these two zeolite membranes will offer essentially no diffusion-controlled selectivity for CO_2 over N_2. At high temperatures, adsorption diminishes and therefore the adsorption-controlled selectivity disappears for these microporous membranes. It is unlikely for other microporous membranes with a pore size larger than FAU type zeolite, such as metal organic framework materials, to exhibit better selectivity and permeance for CO_2/N_2 than those summarized above.

To improve the diffusion controlled CO_2/N_2 selectivity requires further reduction in the membrane pore size. Amorphous silica membranes obtained by the sol-gel method from acid catalyzed polymeric silica sol or by chemical vapor deposition at the intermediate temperature have an ultramicropore structure with pore diameter in the range of 0.3-0.4 nm. These membranes might offer high CO_2/N_2 selectivity at high temperatures if their thermal and hydrothermal stability can be improved. Efforts have been reported to improve the stability of the microporous silica membranes through surface modification or doping of a second metal to the silica framework. Recent work showed that thermally stable microporous silica membranes with a pore diameter of around 0.3 nm can be prepared by a high temperature chemical vapor deposition method [99]. However, the CO_2 permeance of the membrane is too low (about 2×10^{-10} $mol/m^2 \cdot s \cdot Pa$) which is expected from the membrane pore size.

Crystalline zeolite membranes with small pore size offer better chemical stability and more controlled more structure than the amorphous ultramicroporous silica membranes discussed above. Two 8-member-ring zeolites, CHA type (e.g. SAPO-34) and DDR type zeolites have recently attracted much interest as membrane materials for gas separation involving CO_2 [100]. SAPO-34 and DDR zeolites have a pore diameter of about 0.38 and 0.36x0.44 nm, respectively, slightly larger than the kinetic diameter of CO_2 and N_2. SAPO-34 membranes exhibit good separation properties for CO_2/CH_4 mixture separation [100]. However, presence of water in the gas stream has a negative impact on SAPO-34 membrane performance due to the hydrophilic nature of the SAPO-34 framework. DDR zeolite contains pure silica, and, similar to pure silica 10- or 12-member-ring MFI type silicalite and FAU-type dealuminized-Y zeolites, is highly chemically and thermally stable. A 5 µm thick DDR zeolite membrane, possibly containing some microporous intercrystalline defects [94], has CO_2 permeance of about 3×10^{-7} $mol/m^2 \cdot s \cdot Pa$ and CO_2/N_2 selectivity of about 30 at 25 °C [101]. The selectivity and permeance of these membranes can be improved if the membrane thickness is further decreased and the intercrystalline pores of membrane eliminated.

For microporous inorganic membranes there is a limit to improve the CO_2/N_2 selectivity while maintaining high permeance through pore size reduction. Dense, nonporous ceramic membranes are known for their infinitely large selectivity for O_2 over N_2, and high O_2 permeance at temperatures above 700°C. Research efforts on synthesis of dense Li_2ZrO_3 and Li_4SiO_4 membranes for high temperature separation of CO_2 were reported but these membranes exhibit a CO_2/N_2 selectivity of about 5 and CO_2 permeance of 10^{-8} $mol/m^2 \cdot s \cdot Pa$ at 525 °C [102]. It is known that molten carbonate, such as Li_2CO_3/K_2CO_3, can conduct CO_3^{2-} at a very high rate at high temperatures. A metal-carbonate dual-phase membrane was prepared and shown to be able to separate CO_2 from mixture of N_2, CO_2 and O_2 [101].

However the permeation of CO_2 through the metal-carbonate membrane requires the presence of oxygen and the membrane suffers from a stability issue due to metal oxidation and metal-carbonate interaction. These problems can be addressed by replacing the metal phase with a mixed electronic-ionic conducting metal oxide phase [102]. A dual-phase membrane consisting of a molten carbonate ($Li_2CO_3/Na_2CO_3/K_2CO_3$) entrapped in a porous $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ support is perm-selective to CO_2 (with CO_2/N_2 selectivity well above 225) with CO_2 permeance of above $1.0x10^{-8}$ mol/m^2·s·Pa at temperatures above 500 °C. These membranes have potential for pre-combustion CO_2 capture applications, but much more work need to be done to improve the CO_2 permeance.

3.3.2 Theoretical and Experimental Studies on the Mechanism of Gas Separation

Development of membranes that create a step change in performance relative to existing materials presents two complementary challenges. First, a large search space of possible materials must be considered to select a small number of materials that are expected to yield high performance membranes. If the aim is to use zeolites to make a membrane, for example, the identity and chemical composition of the zeolite(s) to be studied must be chosen from among hundreds of possible candidate materials. Second, the physical issues that affect the practical performance of membranes that are fabricated into working devices must be understood and controlled. To continue with the example of a zeolite membrane, the crystal orientation and microstructure of a zeolite film is often decisive in membrane performance. In broad terms, theoretical studies are currently making valuable contributions in the first area (materials selection), while device performance issues are currently most effectively addressed experimentally. Below, the current status of these issues for several different classes of membranes is briefly reviewed.

<u>Nanoporous membranes:</u> The potential for crystalline nanoporous materials to overcome the fundamental selectivity/throughput tradeoff that exists for polymeric membranes is widely known. Extensive experience has been accumulated in fabrication of zeolite membranes [105]. MOFs represent a useful extension of the class of nanoporous materials that can be considered as membranes, but development of MOF membranes is at an early stage of development. Detailed theoretical models show promise for guiding materials selection of MOFs for membrane development [106]. The characteristics of molecular diffusion in nanoporous materials are critical to the performance of membranes grown from these materials, and most information about molecular diffusion in MOFs to date has come from theoretical studies. The development of theoretical models that combine quantum chemistry and force field-based calculations to accurately describe the subtle balance of dispersion forces and framework flexibility effects in MOFs has progressed rapidly in recent years, although this work has been hampered in some instances by the availability of reliable, reproducible experimental data. It appears likely that in the near future it will be possible to use theoretical methods to screen large numbers of MOFs to reliably select which materials have most promise as membrane materials.

When membranes are fabricated based on intergrown thin films of zeolites or MOFs, the microstructure of the resulting films can be critical in the effectiveness of the membrane. Significant progress has been made in controlling film microstructure for some zeolite films [105], but control of these issues for new materials remains a severe challenge. Theoretical models currently contribute little to this challenge.

An attractive alternative to making membranes from intergrown thin films of crystalline materials is to use polymer/filler composites as membranes. These so-called mixed matrix membranes are likely to play an important role in near term technologies because they can be used to manufacture membranes at large scales using minor variations on known approaches [107]. As theoretical methods are used to screen new nanoporous materials, it is becoming possible to consider which polymer/filler combinations will have desirable membrane properties and to focus experimental efforts on these materials [108]. Issues of particle size, particle dispersion, and the interface between filler particles and the polymer matrix are typically critical in the viability of mixed matrix membranes. A significant body of knowledge already exists associated with these issues for nonporous and zeolite filler particles [109]. The use of MOFs as filler particles is relatively new, so these important microstructure-related topics are not yet well understood for MOF/polymer composites.

Dense membranes for high temperature separations: Membranes to separate high temperature syngas can potentially play an important role in CO_2 mitigation within IGCC and other gasification processes. Theoretical approaches based on quantum chemistry calculations are beginning to play a useful role in materials selection for dense metal membranes using both crystalline and glassy metals [110]. Current theoretical approaches focus on predicting the throughput of hydrogen through these dense films. The response of metal films to gas contaminants such as S-containing species remains a critical issue for implementation of these devices, and this topic is currently only accessible via experiments. The fundamental mechanisms of membrane poisoning by these contaminants remain poorly understood; changing this situation could allow significant progress in the development of practical membranes.

Ceramic membranes also show promise for high temperature CO_2 separations. Progress has been made in testing devices made from lithium-based ceramics [111]. These experimental studies have revealed the main physical mechanisms that control CO_2 permeation through these ceramics. Little theoretical work is available on these mechanisms, so theory has not yet played a role in materials selection in this area.

3.3.3 Industrial Applications of Gas Separation Membranes

Membrane gas separation is one of the most significant new unit operations to emerge in chemical industry in the last 40 years. From tentative beginnings in the 1970's, commercial gas separation membranes have evolved to the point where they have gained industrial acceptance in many areas such as nitrogen production, hydrogen separation and natural gas upgrading (Figure 18). In virtually all areas where gas separation membranes are commercial today, they compete with established, well –developed technologies like cryogenic distillation, pressure swing adsorption (PSA) and liquid absorption. Selection of the best technology is always difficult because in practice the specifics of each application, such as product purity, feed composition, utilization patterns, turndown requirements, impurity levels, supply pressure, operating temperature and the relative cost of power and capital all have a significant impact on the selection of the optimal technology and process configuration. This section will highlight the two relevant areas where membranes have been most successful in industrial gas applications.

Membrane air separation is based primarily on the use of composite and asymmetric hollow fiber technology using polymers that permeate oxygen faster than nitrogen. This permits the design of relatively simple cycles that fundamentally require only a compressor and a membrane assembly; nitrogen is the retentate and is obtained at close to compressor discharge pressure while an oxygen rich gas is obtained as low pressure permeate. In principle, it is possible to use membranes to produce .both oxygen and nitrogen. In practice, with current membrane properties, it is much easier to produce high purity nitrogen and hence membranes have been confined largely to nitrogen production.

Figure 18. A membrane plant for natural gas processing (courtesy MTR, Inc.).

In general, the O_2/N_2 selectivities of polymers used in air separation are in the range of 4 - 8 and the permeabilities are in the range of 1 – 20 Barrers. The effective skin thickness achieved in production is in the range of 500 - 2000 Å. Small skin thicknesses are most desirable because they increase membrane productivity (P/t) and permit the use of higher selectivity (but lower permeability) materials. The thin "skin" is always supported on a porous layer which provides structural strength.

The simple, single stage process is best for producing low purity nitrogen while multi-stage processes are better suited at higher purities and large capacities. "Oxygen free" nitrogen can be produced using a hybrid system comprised of a membrane system plus a catalytic de-oxygenation system using hydrogen to remove the residual oxygen.

Oxygen production by membranes has to date seen only limited application and has been confined to small sizes and low purities. This is due to the following important factors:

- The cost of O_2 produced is high.
- Most traditional applications use high purity O_2, but current material selectivities and permeabilities are too low for high purity O_2 production.
- Oxygen is typically produced at low pressure and O_2 compression is expensive.
- The contaminants present in feed air (e.g. CO_2, H_2O) contaminate the product

To produce low cost oxygen at high purity, membranes with very high permeability and selectivity are required. The most common process used for membrane O_2 production is the simple, single stage process in which the O_2 rich permeate is obtained as the product. The lack of membrane materials which simultaneously possess high selectivity and very high permeability has stymied the commercial development of membranes for oxygen production. It is important to note that many industrial gas companies ar developing oxygen transport membranes of the sort described above. For example some, such as Air Products are now in pilot scale testing on the tons per day level.
http://www.airproducts.com/PressRoom/CompanyNews/Archived/2009/21May2009b.htm

<u>CO_2 Removal in Natural Gas Processing</u>**:** The most widely practiced application of membrane processes in natural gas treatment is for CO_2 removal (Figure 19). Cellulose membranes have been used primarily for the past 20+ years and have been now increasingly applied for larger flow rate applications. Recent advances in membrane technology have introduced new commercial membranes in this market space. Specifically, rubbery CO_2 selective membranes (e.g. Polaris from MTR, Inc.) and glassy polymer membranes (e.g. polyimide, perfluoro) have recently been introduced in limited applications in the gas treatment market. These membranes are being tailored to address certain shortcomings of conventional cellulosic membranes such as membrane stability and requirement for substantial pretreatment.

Apart from CO_2 removal from natural gas, two other applications have gained significant traction in natural gas processing and treatment. Membranes are now successfully deployed for nitrogen removal from natural gas and numerous plants are now operating in the US. Also, new membranes have been applied successfully for the separation of heavy hydrocarbons and acid gases such as H_2S and CO_2 from

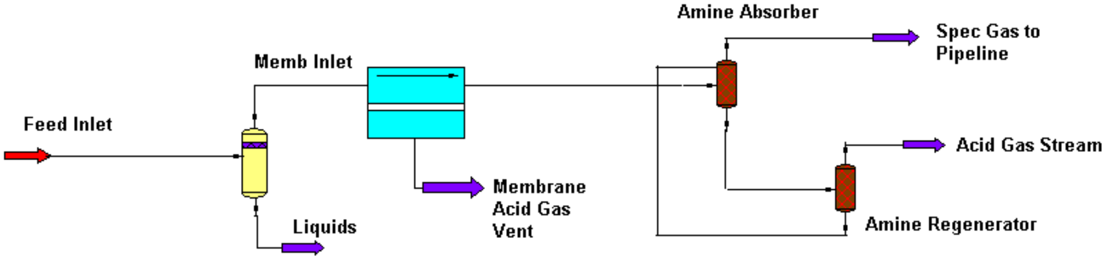

Figure 19**.** Hybrid membrane process for CO_2 removal from natural gas (Courtesy MTR Inc.).

fuel gas used to fuel gas engines and turbines. Fuel gas cleanup reduces emissions and increases operational efficiency of gas engines and turbines which are the work horses for moving natural gas in the pipeline grid. Table 5 provides a summary of typical application conditions for the use of membranes in natural gas processing.

Table 5. **Application of membranes in natural gas processing**

Application	**Species Removed**	**Typical Flow MMSCFD**	**Feed Pr Psig**	**Temperature F**
CO_2 Removal	CO_2	0.5 - 500	100 - 1500	0 - 150
N_2 Removal	N_2	0.2 - 50	100 - 1500	0 - 150
Fuel Gas Conditioning	C2+ hydrocarbons, H_2S, CO_2, Water	0.1 - 100	101 - 1500	0 - 150

4.0 Alternative Gas Separation Pathways

A brief summary is provided here of alternative pathways for CO_2 capture via hydrate formation, and catalytic-based chemical conversions.

4.1 Gas Hydrates

It is well known that CO_2, N_2, O_2 and H_2 are molecules which have the ability to combine with H_2O under proper temperature and pressure conditions to form a crystal known as gas or clathrate hydrate [112, 113]. Water molecules linked through hydrogen bonding enclose the CO_2 molecules in cavities and create guest/host (H_2O) arrangements known as gas or clathrate hydrate crystals (cubic structure). Recently, the use of hydrates for CO_2 capture from flue gas mixtures became of interest [114, 115]. The U.S. Department of Energy proposed a concept for a high-pressure process to recover H_2 and CO_2 from a shifted synthesis gas stream [116, 117]. However, very little data were presented. The hydrate process is able to concentrate a CO_2 containing stream. There remains the CO_2-lean stream, which cannot be treated through hydrate formation since it would be rich in either N_2 or H_2 and the required pressures would be very high. Thus, the hydrate process should be coupled with another, highly selective process for CO_2 capture.

4.2 Chemical Conversion

To date the efforts to convert CO_2 from the manufacturing sector into useful products have been rather limited. Thermodynamic considerations show that it is impossible to get more energy from CO_2 reduction products than needed to reduce CO_2 into products. As such, all approaches to CO_2 conversion to value added products employ energy from renewable sources, e.g. photocatalytic reduction, CO_2 as a solvent, CO_2 as a polymer precursor, etc.

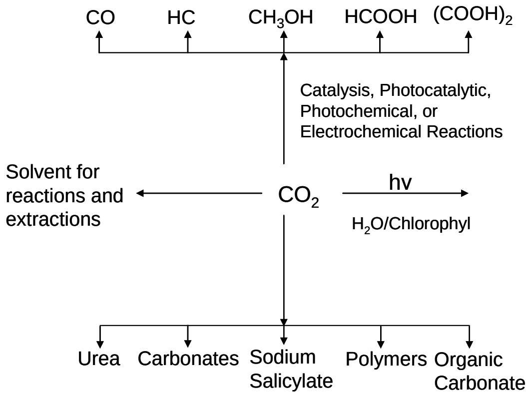

Figure 20. Conversion of CO_2 to various products.

The use of CO_2 as a reagent in organic synthesis is receiving renewed attention. Another highly desirable approach to convert CO_2 into useful products is artificial photosynthesis. In this scenario, CO_2 produced from various sources can be efficiently converted to hydrocarbons, alcohols of synthesis gas employing solar energy. This approach will create an artificial CO_2 cycle and reduce the need for CO_2 capture and sequestration. The photochemical CO_2 reduction employing homogeneous catalysts has been the subject of intense interest for a number of years now [118, 119]. However, the stability of CO_2 makes economical utilization of carbon dioxide as a feedstock for fuels or chemicals a formidable challenge.

Since CO_2 lies in a deep energetic well of stability, the reduction process will be energy intensive and for significant round-trip cycle efficiency requires a renewable energy input. The voltage and free energy required for several CO_2 reduction processes can be provided by using 'direct' electrochemistry with concomitant water splitting or by use of hydrogen as a chemical reductant. To create fuels or chemical feed stocks with C-2 or greater from CO_2, electrochemical reduction steps must be coupled to C-C bond formation chemistry. Two dominant pathways are identified that can potentially facilitate this type of reaction - direct electrocatalytic conversion where reactions occur between adsorbed species on a surface, typically metallic, that catalyzes reactions and electrochemically mediated processes using organometallic complexes.

A number of mechanistic pathways utilizing heterogeneous catalysis are available for conversion of CO_2 to useful feedstocks. The most direct and extensively studied of these involves hydrogenative conversion of CO_2 to methanol. Efficient heterogeneous catalysts based on metals and their oxides, in particular the combination of copper and zinc oxide have been developed for this conversion. Another mechanism, known as the Sabatier reaction or Sabatier process involves the reaction of hydrogen with carbon dioxide at elevated temperatures and pressures in the presence of a nickel catalyst to produce methane and water. Optionally ruthenium on aluminum oxide makes a more efficient catalyst [120]. CO_2 reduction to CO can be achieved by the reverse Boudouard reaction via the thermal reaction of carbon dioxide with carbon, or coal itself. This process has an advantage over the steam reforming of coal, which is somewhat less endothermic (31.3 kcal mol^{-1}), in that it allows for the recycling of CO_2. Another mechanistic pathway optimizes the use of natural gas resources (which generally contain 5 to 50 % CO_2) and concurrently converts CO_2 to *syngas* via reaction of CO_2 with natural gas or other hydrocarbon sources. This reaction is carried out commercially at temperatures around 800-1000 °C using catalysts based on nickel and other metals (Ni/MgO, $Ni/MgAl_2O_4$, Ni/Al_2O_3, Rh/NaY, Rh/Al_2O_3, etc) [121-123]. CO_2 is used as a feedstock reacted with ammonia under pressure with no catalyst present to produce urea [124]. This reaction is practiced in a large scale and currently close to 80 Mt of CO_2 is consumed annually.

5.0 Summary and Technical Challenges

As with the March 2009 workshop on carbon capture co-sponsored by BES and FE [125], several overall common scientific and technologic themes have been highlighted in this factual document that require near-term attention in order to stimulate transformative breakthroughs in mitigating carbon emissions. These include; (a) fundamental understanding of gas-host interactions, (b) need to measure and understand in greater detail key thermodynamic, kinetic, chemical and structural characteristics of the current suite of available materials, (c) discovery of entirely new materials for carbon capture and oxygen separation from air, (d) discovery of capture materials that can be regenerated with minimal energy use, perhaps through mechanisms other than thermal or pressure swings, and (e) implementation of new approaches to theory, modeling and simulation that accelerate the scale-up. A synergistic research portfolio involving novel experiments, synthesis, analytical and characterization methods in concert with molecular-level simulations is needed to fill key knowledge gaps in our fundamental understanding of materials properties and reaction chemistry. Science discovery should keep pace with the expected timeline for commercial deployment of capture and storage as outlined in Fig. 21 [126].

In the context of Basic Energy Sciences, five broad areas are defined that could afford new research opportunities to the materials and chemistry community. These are liquid absorbents, solid absorbents, membranes, gas hydrate separation and catalytic materials/reactions. Each of these has varying applicability to the three main carbon capture technologies currently being investigated – post-, pre-, and oxy-combustion.

Liquid absorbent-based CO_2 capture involves chemical or physical sorption of CO_2 from flue gas into a liquid carrier. Solvent-based systems, such commercially available amine-based systems, are being used today for scrubbing CO2 from industrial flue gases and process steams. However, scaling this type of CO_2 capture methodology to the size required for processing large volumes of CO_2 has not been achieved. Research efforts on liquid absorbents need to focus on new solvents that are thermally stable to high temperatures, chemically stable in flue gas conditions, have a high CO_2 loading capacity, minimize regeneration energy, exhibit fast reaction kinetics, are non-corrosive and are cost effective. Scientific breakthroughs may be realized through exploration of new amine-based chemistry, novel ionic liquids and ionic-liquid supported polymeric membranes, especially for materials that can be regenerated with minimal parasitic energy.

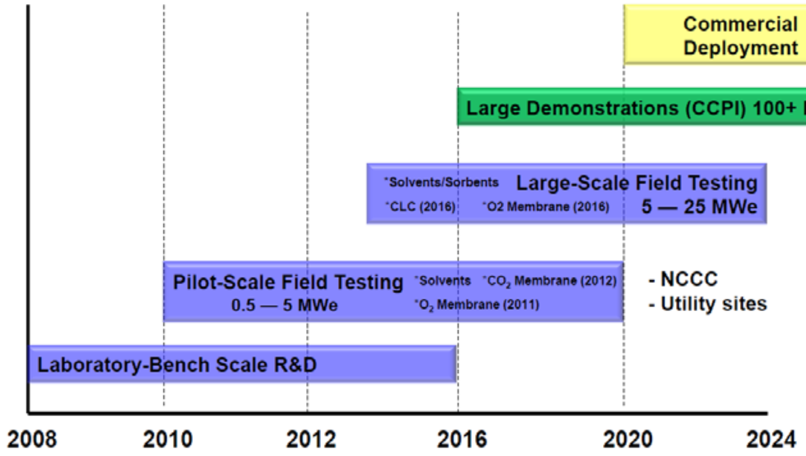

Figure 21. R & D timeline for commercial deployment of carbon capture [126].

Solid absorbents such as metal-organic and zeolite imidazolate frameworks have highly desirable properties such as microporosity, high surface areas, and exceptional thermal and chemical stability, making them potentially ideal for gas separation applications. Scaling to "real world" conditions is recognized as a major obstacle in the deployment of solid sorbents. Additionally, fundamental research is needed to identify new methods for releasing CO_2 from the solid sorbents (e.g. microwave, electrical or optical), and to develop novel functionalization schemes of the pore walls that improve thermal and chemical stability (particularly during pressure drops), diffusivity and sorptive selectivity.

Membranes for CO_2 separation are, in principle, simple to operate – i.e. no chemical reactions to track and no moving parts. Currently available membranes have a tolerance to high levels of wet acid gases, are compact and modular with a small footprint and require relatively low energy. However a number of technology challenges remain including the need to handle low flue gas CO_2 partial pressures, withstand the deleterious effects of particulate matter degradation of membrane performance and life, reduced cost and scale-up for large volumes of CO_2. For post-combustion capture, advanced membrane research targets include the design and synthesis of new materials that have high CO_2/N_2 selectivity and permeability which will require tailoring the pore size and distribution in ways that do not degrade gas permeance, chemically stabilize membranes especially in the presence of SO_2, and control the microstructure and crystal orientation of thin-film membranes. For oxy-combustion materials that would allow for low cost separation of oxygen from air are needed.

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APPENDIX B: CARBON CAPTURE: BEYOND 2020

WORKSHOP AGENDA

Carbon Capture: Beyond 2020

Sponsored by
The Office of Basic Energy Science and the Office of Fossil Energy

March 4-5, 2010

Gaithersburg Marriott Washingtonian Center
9751 Washingtonian Boulevard
Gaithersburg, MD

AGENDA

Wednesday Evening – March 3rd

6:00–7:00	Pre-meeting Social Reception in the Foyer (All)
7:00–9:00	Working Dinner for Executive Committee in Salon D (Invitation Only)

Thursday – March 4th

7:00–8:00	Continental Breakfast in Foyer
PLENARY SESSION:	Moderators – Paul Alivisatos and Michelle Buchanan (Salon E, F, and G)
8:00–8:05	Welcome and Opening Comments – Harriet Kung
8:05–8:25	William Brinkman, Director, Office of Science
8:25–8:45	Victor Der, Principal Deputy Assistant Secretary for Fossil Energy
8:45–9:30	Edward Rubin, Carnegie Mellon – *Challenges and Opportunities for Advanced Carbon Capture*
9:30–9:50	Break
9:50–10:35	Abhoyjit Bhown, EPRI – *Status of Post-Combustion CO2 Capture Technologies*
10:35–11:20	Rodney Allam, NET Power, LLC – *Carbon Dioxide Capture Using Oxy-Fuel Systems*
11:20–12:00	Charge to Breakout Groups
12:00–1:00	Working Lunch in Breakout Groups
1:00–3:00	Work in Breakout Groups
	Group 1. **Membranes** (Salon D) **Group 2.** **Solid Sorbents** (Salon C) **Group 3.** **Liquids-Based Absorption** (Boardroom/Rio Suite) **Group 4.** **Cross-Cutting Analysis Tools** (Salon A) **Group 5.** **Cross-Cutting Computation** (Salon B)
3:00–3:30	Break
3:30–5:30	Work in Breakout Groups
6:00	Working Buffet Dinner (All)

Friday – March 5th

7:00–8:00	Continental Breakfast in Foyer
8:00–9:30	Preliminary Report from Breakout Groups (Salon E, F, G)
9:30–10:00	Break
10:00–12:00	Work in Breakout Groups
12:00–1:00	Working Lunch
1:00–3:00	Work in Breakout Groups
3:00–3:15	Break
3:15–5:00	Reports from Breakout Groups (Salon E, F, G)
5:00	Departure of Workshop Participants (except Executive Committee and designated writers)
6:00	Working Dinner for Executive Committee and Writers

Saturday – March 6th

8:00–12:00	Workshop Report Preparation
12:00–1:00	Lunch
1:00	Workshop Ends

APPENDIX C: CARBON CAPTURE: BEYOND 2020 WORKSHOP ATTENDEES

LIQUIDS-BASED ABSORPTION PANEL LEADS: WILLIAM SCHNEIDER, NOTRE DAME UNIVERSITY, WSCHNEIDER@ND.EDU PETER CUMMINGS, VANDERBILT UNIVERSITY, PETER.CUMMINGS@VANDERBILT.EDU					
NAME	**INSTITUTION**	**DISCIPLINE**	**TOPIC AREA**	**EMAIL ADDRESS**	**ACCEPT/DECLINE**
Richard Noble	Colorado Univ	Chem Engineering	Separations; ionic liquids; membranes	nobler@colorado.edu	Accept
John Kitchin	Carnegie-Mellon	Chem Engineering	novel amine electroChem CO2 separation	jkitchin@andrew.cmu.edu	Accept
Michael Malone	Univ of Massachusetts	Chem Engineering	separations; process optimization	mmalone@umass.edu kimfill@research.umass.edu	Accept
Bruce Kay	PNNL	Chem Physics	interfacial chemistry; aqueous interfaces	bruce.kay@pnl.gov	Accept
John Hemminger	UC Irvine	Chemistry	aqueous interfaces; interface science; spectroscopy	jchemmin@uci.edu	Accept
Joan Brennecke	Notre Dame	Chem Engineering	thermodynamics; phase equilibria; Ionic liquids	jfb@nd.edu	Accept
Ellen Stechel	SNL		CO2 capture and conversion strategies	ebstech@sandia.gov	Accept
Carol Fierke	Univ of Michigan		biochemistry of carbonic anhydrase chemistry	fierce@umich.edu	Accept
Roger Aines	LLNL		engineering of carbonic anhydrase chemistry	aines1@llnl.gov	Accept
Jeff Siirola	Eastman Kodak		process engineering and optimization	siirola@eastman.com	Accept
Abhoyjit Bhown	EPRI		CO2 capture issues	abhown@epri.com	Accept
Evan Granite	NETL			evan.granite@netl.doe.gov	Accept

MEMBRANES

PANEL LEADS:
BENNY FREEMAN, UNIVERSITY OF TEXAS AT AUSTIN, FREEMAN@CHE.UTEXAS.EDU
SAMUEL STUPP, NORTHWESTERN UNIVERSITY, S-STUPP@NORTHWESTERN.EDU

NAME	INSTITUTION	DISCIPLINE	TOPIC AREA	EMAIL ADDRESS	ACCEPT/DECLINE
Ed Sanders	Air Liquide			Ed.Sanders@airliquide.com	Accept
Tim Merkel	Membrane Technology & Research (MTR)			Tcmerkel@mtrinc.com	Accept
Ken McCarley	ConocoPhillips			Ken.C.McCarley@ConocoPhill.com	Accept
Lora Toy	Research Triangle Institute (RTI)			ltoy@rtl.org	Accept
Bill Koros	Georgia Tech			William.koros@che.gatech.edu	Accept
Jerry Lin	Arizona State Univ			Jerry.Lin@ASU.edu	Accept
Jim McGrath	Virginia Tech			Jmcgrath@vt.edu	Accept
Harry Cordatos	United Technologies Research Center			CordatH@utrc.utc.com	Accept
Francesco Fornasiero	Lawrence Livermore National Laboratory			fornasiero1@llnl.gov	Accept
Sossina Haile	Cal Tech		Ceramics	smhaile@caltech.edu	Accept
Ralph Nuzzo	Illinois		Inorganic chemist	r-nuzzo@illinois.edu	Accept
Ken Poeppelmeier	Northwestern Univ			krp@northwestern.edu	Accept
Alexei Sokolov	ORNL	Polymer Chemistry		sokolovap@ornl.gov	Accept
Anita Hill	CSIRO			Anita.Hill@csiro.au	Accept
Kathryn Berchtold	LANL			berchtold@lanl.gov	Accept
David Luebke	NETL	Chem Engineering	CO2 capture science and materials	david.luebke@netl.doe.gov	Accept

Solid Sorbents

Panel Leads:
Omar Yaghi, University of California at Los Angeles, yaghi@chem.ucla.edu
Chris Murray, University of Pennsylvania, cbmurray@sas.upenn.edu

Name	Institution	Discipline	Topic Area	Email Address	Accept/Decline
Seth Cohen	UC San Diego		reactive MOFs; proposed writer	scohen@ucsd.edu	Accept
Guido Pez	Air Products		oxygen generation and separations; proposed writer	pezgp@ptd.net	Accept
Yuri Gogotsi	Drexel Univ		nanoporous carbons; proposed writer	gogotsi@drexel.edu	Accept
Mike Stiegerwald	Columbia Univ	Chemistry	novel nanoscale metal oxides synthesis and processing including zirconates and hafnium oxide; alternate proposed writer	mls2064@columbia.edu	Accept
Jeff Long	UC Berkeley		MOFs for separations (nitrogen, hydrogen, and CO2)	jrlong@berkeley.edu	Accept
Sheng Dai	ORNL		Carbon and functionalized materials for separations plus ionic liquids	dais@ornl.gov	Accept
Radu Custelcean	ORNL		External field assisted separations and Inorganic materials for separations	custelceanr@ornl.gov	Accept
Lynn Schneemyer				schneemeyer@mail.montclair.edu	Accept
Cynthia Friend	Harvard Univ			cfriend@seas.harvard.edu	Accept
Henry Pennline	NETL			henry.pennline@netl.doe.gov	Accept

CROSS-CUTTING ANALYSIS TOOLS PANEL LEADS: MURRAY GIBSON, ARGONNE NATIONAL LABORATORY, JMGIBSON@APS.ANL.GOV MARTIN ZANNI, UNIVERSITY OF WISCONSIN AT MADISON, ZANNI@CHEM.WISC.EDU					
NAME	**INSTITUTION**	**DISCIPLINE**	**TOPIC AREA**	**EMAIL ADDRESS**	**ACCEPT/DECLINE**
Wendy Mao	Stanford Univ	Geological and Environmental Sciences	high-pressure geophysics; volatiles in hydrogen storage applications	wmao@stanford.edu	Accept
Phil Grandinetti	Ohio State Univ			grandinetti@me.com	Accept
Yves Chabal	Univ of Texas-Dallas			chabal@utdallas.edu	Accept
Alex Harris	BNL			alexh@bnl.gov	Accept
Taner Yildirim	Univ of Pennsylvania			taner@seas.upenn.edu	Accept

CROSSCUT COMPUTATION

PANEL LEADS:
BEREND SMIT, UNIVERSITY OF CALIFORNIA AT BERKELEY, BEREND-SMIT@BERKELEY.EDU
PAULETTE CLANCY, CORNELL UNIVERSITY, PQC1@CORNELL.EDU

NAME	INSTITUTION	DISCIPLINE	TOPIC AREA	EMAIL ADDRESS	ACCEPT/DECLINE
Michael Deem	Rice Univ	BioChem; Genetic Engineering;		mwdeem@rice.edu	Accept
Brian Anderson	West Virginia Univ	Chem Engineering		brian.anderson@mail.wvu.edu	Accept
Maciej Haranczyk	Lawrence Berkeley National Laboratory	Computational Research		mharanczyk@lbl.gov	Accept
R. Krishna	Univ of Amsterdam	Chem Engineering		r.krishna@uva.nl	Accept
Laura Gagliardi	Univ of Geneva	Physical Chem			Accept

OTHERS

NAME	INSTITUTION	DISCIPLINE	TOPIC AREA	EMAIL ADDRESS	ACCEPT/DECLINE
William Brinkman	DOE, Office of Science	Director	Plenary session	Bill.Brinkman@science.doe.gov	Accept
James Markowsky	DOE, Fossil Energy	Asst Secretary	Plenary session	james.markowsky@hq.doe.gov	Accept
Edward Rubin	Carnegie Mellon		Plenary session	rubin@cmu.edu	Accept
Abhoyjit Bhown*	EPRI		Plenary session	abhown@epri.com	Accept
Rodney Allam	NET Power, LLC		Plenary session	rjallam@hotmail.co.uk	Accept
Michelle Buchanan	ORNL		Workshop Co-Chair	buchananmv@ornl.gov	Accept
Paul Alivisatos	LBNL		Workshop Co-Chair	APAlivisatos@lbl.gov	Accept
Pat Dehmer	DOE, Office of Science			patricia.dehmer@science.doe.gov	Accept
Ben Brown	DOE, Office of Science			ben.brown@science.doe.gov	Accept
David Thorn	LANL		Observer	dthorn@lanl.gov	Accept
Phil Britt	ORNL		Observer	brittpf@ornl.gov	Accept
Bruce Garrett	PNL		Observer	bruce.garrett@pnl.gov	Accept
Dave Cole	ORNL		Observer	colder@ornl.gov	Accept
Mark Hartney	ARPA-E		Observer	mark.hartney@hq.doe.gov	Accept
Gerry Stokes	BNL		Observer	stokes@bnl.gov	Accept
Jeff Fitts	BNL		Observer	fits@bnl.gov	Accept
Richard Doctor	ANL		Observer	rdoctor@anl.gov	Accept
Jared Ciferno	NETL		Observer	jared.ciferno@netl.doe.gov	Accept
Rich Calabrees	DOE, Fossil Energy		Observer	Richard.calabrese@hq.doe.gov	Accept
Miles Palmer	NET Power, LLC		Observer	miles.palmer@palmerlabs.com	Accept
Scott Litzelman	ARPA-E		Observer	scott.litzelman@hq.doe.gov	Accept
Karma Sawyer	ARPA-E		Observer	karma.sawyer@gmail.com	Accept

*Dual role – also in Liquids-Based Absorption group