Direct Air Capture of CO$_2$ with Chemicals

A Technology Assessment for the APS Panel on Public Affairs

June 1, 2011

Report Committee

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Executive Summary

This report explores direct air capture (DAC) of carbon dioxide (CO$_2$) from the atmosphere with chemicals. DAC involves a system in which ambient air flows over a chemical sorbent that selectively removes the CO$_2$. The CO$_2$ is then released as a concentrated stream for disposal or reuse, while the sorbent is regenerated and the CO$_2$-depleted air is returned to the atmosphere.

To guide the reader to an understanding of the factors affecting costs, a benchmark system is introduced that could be built today. With optimistic assumptions about some important technical parameters, the cost of this system is estimated to be of the order of $600 or more per metric ton of CO$_2$. Significant uncertainties in the process parameters result in a wide, asymmetric range associated with this estimate, with higher values being more likely than lower ones. Thus, DAC is not currently an economically viable approach to mitigating climate change. Any commercially interesting DAC system would require significantly lower avoided CO$_2$ costs, and thus would likely have a design very different from the benchmark system investigated in this report. This report identifies some of the key issues that need to be addressed in alternative designs.

The physical scale of the air contactor in any DAC system is a formidable challenge. A typical contactor will capture about 20 tons of CO$_2$ per year for each square meter of area through which the air flows. Since a 1000-megawatt coal power plant emits about six million metric tons of CO$_2$ per year, a DAC system consisting of structures 10-meters high that removes CO$_2$ from the atmosphere as fast as this coal plant emits CO$_2$ would require structures whose total length would be about 30 kilometers. Large quantities of construction materials and chemicals would be required. It is likely that the full cost of the benchmark DAC system scaled to capture six million metric tons of CO$_2$ per year would be much higher than alternative strategies providing equivalent decarbonized electricity. As a result, even if costs fall significantly, coherent CO$_2$ mitigation would result in the deployment of DAC only after nearly all significant point sources of fossil CO$_2$ emissions are eliminated, either by substitution of non-fossil alternatives or by capture of nearly all of their CO$_2$ emissions.

Nonetheless, DAC is one of a small number of strategies that might allow the world someday to lower the atmospheric concentration of CO$_2$. The wide-open science and engineering issues that will determine ultimate feasibility and competitiveness involve alternative strategies for moving the air and alternative chemical routes to sorption and regeneration.

Ultimate judgments about the future role for DAC and its future cost are necessarily constrained by the scarcity of experimental results for DAC systems. No demonstration or pilot-scale DAC system has yet been deployed anywhere on earth, and it is entirely possible that no DAC concept under discussion today or yet to be invented will actually succeed in practice. Nonetheless, DAC has entered policy discussions and deserves close analysis. This report provides insights into how DAC relates to greenhouse gas emissions.

This report was prepared for the APS Panel on Public Affairs (POPA). POPA routinely produces reports on timely topics so as to inform the debate with the perspectives of physicists and other scientists working in the relevant issue areas, including energy and the environment. Most reports prepared for POPA are policy studies, often making policy recommendations and suggesting priorities for research support. This report, by contrast, is a technology assessment and contains no policy or funding recommendations. The analysis is the outcome of a two-year study conducted by a 13-member committee whose members work in industry, academia, and national and government laboratories.

Context: Global net-negative CO$_2$ emissions and the potential role of DAC

CO$_2$ removal strategies such as DAC might allow the world to pursue a strict stabilization target for the CO$_2$ concentration, by first overshooting the target and later approaching the target from above via net negative global emissions. The latter part of an overshoot requires a sustained period of net-negative global CO$_2$ emissions. To contribute, DAC would need to be applied on a large scale, and to be accompanied by a reliable system for long-term storage of the captured CO$_2$. Some century-scale economic models of global CO$_2$ emissions feature such overshoot trajectories. Given the large uncertainties in the future cost of DAC and other CO$_2$ removal strategies, such approaches should be viewed with extreme caution.

DAC could at best be deployed slowly. Therefore, it is not at all matched to the task of reacting quickly to an abrupt climate emergency, for which the required rates of construction of facilities above and below ground are implausible.

If humanity someday chooses to reduce the atmospheric CO_2 concentration gradually, DAC would compete with two terrestrial biological strategies: 1) afforestation, reforestation, and other measures that store additional carbon on the land, and 2) capture of CO_2 from bioenergy facilities, such as biomass power plants. DAC might well be deployed in parallel with these biocapture strategies and still other strategies for removing CO_2 from air. This report focuses on only the DAC alternative, with the expectation that other alternatives will eventually receive comparable critical attention.

DAC costing

To evaluate a large DAC facility that could conceivably be built today, this report uses a simplified costing methodology applied in industry to early-stage projects. The benchmark DAC system is assumed to have a capacity of 1 $MtCO_2$/yr and to absorb CO_2 by passing air over a solution of sodium hydroxide in a counter-current, closed system. The sodium hydroxide solution containing sodium carbonate is then cross-reacted with calcium hydroxide to form calcium carbonate as a precipitate. The solid calcium carbonate is decomposed in a natural-gas-fueled, oxygen-fired kiln, with capture of the released CO_2. The capital cost is estimated to be 2.2 billion dollars, a normalized cost of $2200/(tCO_2$/yr). Capital recovery contributes 60% of the $600/tCO_2$ estimated avoided cost.

For the sake of comparison, using the same methodology the avoided cost for "post-combustion capture" (PCC) of CO_2 from the flue gas of a reference coal power plant is estimated. In the reference PCC system the CO_2 is 300 times more concentrated and the CO_2 removal rate is about three times larger than in for the benchmark DAC system. Relative to the benchmark DAC system, the normalized capital cost for the reference PCC system is estimated to be $180/(tCO_2$/yr), twelve times smaller, and the total avoided cost for capture is estimated to be about $80/tCO_2$, about eight times smaller. Since the total cost includes both operating and capital costs, evidently the operating cost ratio for the two systems is less disadvantageous to the benchmark DAC system than the capital cost ratio. One reason the ratio of operating costs is smaller than the ratio of capital costs is that the assumed energy requirements for the DAC system are optimistic. For example, DAC electricity demand includes fan power to move the air, which is proportional to the pressure drop through the contactor, and the pressure drop assumed in the cost calculation is at the very low end of a credible range for the benchmark system.

The capacity to estimate future DAC costs is limited. Costs could fall as a result of technological learning and with the introduction of fundamentally new ideas. On the other hand, industry experience suggests that cost estimates for any system rise after the completion of pilot plant operations, when the necessary compromises in materials choices, process conditions, component efficiencies, and component lifetimes are taken into account.

The cost estimates in this report are *capture* costs. They do not include the cost of dealing with CO_2 beyond the boundary of the capture facility. Specifically, the costs of sequestering the captured CO_2 from the atmosphere have not been estimated. The principal sequestration strategy under discussion today is injection of CO_2 in geological formations for multi-hundred-year storage. The cost of geological storage is expected to be smaller than the capture cost even for capture from flue gas, but its commercialization at very large scale will require the resolution of formidable reservoir-engineering, regulatory, and public acceptance challenges. It was beyond the scope of this report to investigate post-capture management of CO_2 in any detail.

Net-carbon considerations and centralized emissions of CO_2

All air capture strategies are strongly constrained by the need to remove more CO_2 from the atmosphere than one emits to the atmosphere during the capture process—the "net-carbon" problem. The benchmark DAC system studied in this report is seen to be tightly constrained by net-carbon considerations. For illustrative purposes, the benchmark system assumes that the natural-gas-derived CO_2 emissions are captured at the kiln and then combined with the CO_2 removed from the air. For each ten CO_2 molecules removed from the atmosphere by the sodium hydroxide, about four molecules are released by combustion of natural gas at the kiln, so that 14 CO_2 molecules need to be sequestered.

The benchmark system also assumes that the electricity required for fans, pumps, compressors, and other devices is provided from the average US power grid, which has substantial carbon intensity. As a result, for each ten CO_2 molecules removed from the atmosphere by the DAC system, three CO_2 molecules are emitted to the atmosphere at distant power plants, so that total capture costs are spread over seven-tenths as much captured CO_2 as would have been the case if the electricity had been produced without CO_2 emissions. Indeed, if the power required for the fans were at the high end of the credible range and the power were provided by the same grid, fossil emissions for that power would offset the full amount captured, driving the cost of avoided CO_2 emissions to infinity. Only stringent

combinations of a small pressure drop through the contactor and low-carbon power are consistent with a viable DAC system, from the perspective of net carbon.

Even low-carbon energy sources for DAC are constrained as long as DAC facilities are located within a regional energy system that is not fully decarbonized. Any low-carbon energy source dedicated to a DAC system could instead be used to displace high-carbon centralized sources in the region. Diversion of low-carbon energy supply into DAC and away from its usual decarbonization assignments will be beneficial from a carbon mitigation perspective only in special circumstances. In general, one should expect coherent CO$_2$ mitigation to produce minimal deployment of DAC until CO$_2$ emissions have been nearly eliminated at all large sources of centralized emissions.

Compensating for decentralized emissions

DAC may have the potential to compensate for some decentralized CO$_2$ emissions. However, for at least the next few decades, unless there are dramatic cost reductions, direct air capture can be expected to be substantially more expensive than many other currently available options for reducing decentralized emissions, including 1) substantial improvement of end-use efficiency in all sectors of the economy, 2) electrification of the present direct uses of fossil fuels, accompanied by decarbonization of electricity, and 3) substitution of low-carbon fuel, biologically derived or produced in some other way. As a result, this report provides no support for arguments in favor of procrastination in dealing with climate change that are based on the imminent availability of DAC as a compensating strategy. The pursuit of many currently promising mitigation options deserves higher priority.

Understanding the costs of direct air capture will illuminate a ceiling on costs for mitigation and adaptation. When the cost of some mitigation or adaptation measure exceeds the cost of CO$_2$ removal from the atmosphere, it will be more cost-effective to remove the carbon from the atmosphere after it has been emitted than to prevent its emission in the first place. It is conceivable that some mitigation options that today appear to be very costly may never be needed if operable DAC systems become available.

Toward lower costs

A substantial portion of this report is devoted to indicating DAC systems that could have the potential to lead to lower costs. Such systems would need to differ radically from the benchmark system. Costs for DAC will not fall substantially through incremental improvements in present-day technology, as improvements in one process step may create additional challenges in other process steps or simply lead to trade-offs between capital and operating cost without reducing the cost of the overall process. A trade-off explored repeatedly in this report, for example, exchanges stronger, more efficient binding of CO$_2$ in the capture reaction for greater energy requirements for regeneration.

Lower costs will require substantial improvements in both components and systems. Systems based on cross-current flow in open systems or based on sorbents chemically bonded to a rigid substrate may have potential. Cycles based on new sorbents could come closer to the thermodynamic minimum than the particular sodium hydroxide cycle studied in the benchmark system. Transformational changes will likely require the integration of achievements in several fields of materials science, as well as in chemical and process engineering.

Ultimately, any full-cycle direct air capture process faces the major challenge of operating effectively and efficiently over hundreds to thousands of consecutive cycles.

Pedagogy

The goal of this report is to enable scientifically literate non-specialists to think independently about DAC, whether they are primarily interested in advancements in DAC technology or in placing DAC in a policy context. Throughout, the report seeks to demystify, to explain unfamiliar vocabulary, and to work through representative calculations.

Key Messages

Implications of direct air capture of CO$_2$ by chemicals (DAC) for climate and energy policy

- DAC is not currently an economically viable approach to mitigating climate change.

- In a world that still has centralized sources of carbon emissions, any future deployment that relies on low-carbon energy sources for powering DAC would usually be less cost-effective than simply using the low-carbon energy to displace those centralized carbon sources. Thus, coherent CO$_2$ mitigation postpones deployment of DAC until large, centralized CO$_2$ sources have been nearly eliminated on a global scale.

- DAC may have a role to play eventually in countering emissions from some *decentralized* emissions of CO$_2$, such as from buildings and vehicles (ships, planes) that prove expensive to reduce by other means.

- Given the large uncertainties in estimating the cost of DAC, century-scale economic models of global CO$_2$ emissions that feature "overshoot trajectories" and rely on DAC should be viewed with extreme caution.

- High-carbon energy sources are not viable options for powering DAC systems, because their CO$_2$ emissions may exceed the CO$_2$ captured.

- The storage part of CO$_2$ capture and storage (CCS) must be inexpensive and feasible at huge scale for DAC to be economically viable.

- This report provides no support for arguments in favor of delay in dealing with climate change that are based on the availability of DAC as a compensating strategy.

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Preface

The world has begun to take the proposition seriously that the unconstrained burning of fossil fuels endangers human well-being. The fossil fuel enterprise transfers carbon atoms from deep underground to the atmosphere, where they add to the background level of carbon dioxide and modify climate. A reasonable question is widely asked: Why not learn how to remove carbon dioxide from the atmosphere, thus tackling the problem at the point where the damage is done? Why not work toward the goal of being able to produce, at some future time, a net flow of carbon atoms *from* the atmosphere, so as to undo some of the emissions that have already occurred, and those that lie ahead?

This report explores one of the potential CO_2 removal strategies: direct air capture (DAC) of CO_2 with chemicals. The reader should imagine ambient air flowing over a chemical sorbent that selectively removes the CO_2, and then a subsequent step of desorption that regenerates the sorbent and provides a concentrated stream of CO_2 for disposal or reuse. The wide-open science and engineering issues involve alternative strategies for moving the air and alternative chemical routes to sorption and regeneration.

The possibility of CO_2 removal from the atmosphere is already embedded in some climate policy studies in the form of "overshoot trajectories." Such trajectories result if the world or a country accepts a target for stabilizing the CO_2 concentration at some low level, but sets a course that allows the concentration first to overshoot the target and then to approach to the target from above. The underlying assumption is that negative emissions technology will be cost-effective at large scale at a future time. DAC is a specific strategy that could contribute negative emissions to an overshoot trajectory, and this report is one of the first detailed investigations of the extent to which a specific CO_2 removal strategy is practicable and affordable.

Human beings may wish to cancel some or all future fossil fuel emissions and even to undo past emissions. But wishing is not doing. Using chemicals to remove CO_2 directly from the air at large scale appears to be extremely difficult. The principal reason for this difficulty is that CO_2 is such a dilute constituent of air—only one molecule in 2500 in air is CO_2. Removal of CO_2 from air with chemicals is physically possible, but nonetheless no large-scale system for direct capture with chemicals has yet been deployed anywhere on earth. Indeed, no such scheme has been yet subject to a thorough and wide-ranging evaluation. This report explains some of the reasons why the task appears to be formidable and suggests some of the research directions that might result in demonstrations of technical viability and reductions in costs.

This report is written for the scientifically literate non-expert, not for the specialist. A broad audience of scientists and engineers is targeted to encourage expansion of the limited technical discussion that has occurred to date. The premise of this report, with its emphasis on pedagogy, is that one reason for the current state of affairs is that the underlying science and engineering has been inaccessible. The objective is to provide the background that can allow the reader to engage.

The second audience is the policymaker. The policymaker needs to understand the basis for the judgment in this report that, given what is now known, direct air capture with chemicals will not compete over the next few decades with the currently promising mitigation options, including low-carbon electric power production and transportation, end-use efficiency in buildings and appliances, industrial efficiency, forest protection, and deliberate enhancement of biological carbon storage on the land. The report also provides guidance regarding important areas for research.

An additional reason to improve understanding of the costs of direct air capture is to illuminate the possibility of a ceiling on costs for mitigation and adaptation. When the cost of some mitigation or adaptation measure exceeds the cost of CO_2 removal from the atmosphere, it will be more cost-effective to remove the carbon from the atmosphere after it has been emitted than to prevent its emission in the first place. Some mitigation options that today appear to be very costly may never be needed.

The intention in this report is to call attention to real difficulties and discernable opportunities. The report explains how scientists think about direct air capture, with the goal of helping readers make their own judgments.

Scope and structure of the report

Chapter 1 provides the quantitative context for DAC. It begins with a brief introduction to the most relevant environmental science. It introduces the vexing question of "net carbon" - to what extent will the objective of CO_2 removal be undone by the CO_2 emissions associated with getting the job done? It explains that DAC is one of several strategies whose objective is carbon dioxide removal from air, notably including strategies that exploit the ability of plants to remove CO_2 from the air by photosynthesis. Chapter 1 concludes with a framework for thinking about how costs determine the possible roles of DAC in mitigating climate change.

Chapters 2 and 3 comprise the report's detailed assessment of DAC. Chapter 2 inspects the present and Chapter 3 asks what the future could bring. Chapter 2 shows that much can be learned about DAC from today's efforts in industrial CO_2 capture. One scheme for capturing CO_2 from the flue gas of a coal-fired power plant is compared in technical detail with one particular direct air capture scheme. Their costs are estimated using a common methodology and assuming each was built today.

Chapter 3 suggests several avenues to lower costs for direct air capture in the future. Lower costs will require qualitative improvements in components and systems, such as new binding chemistries based on mimicry of photosynthesis and new systems based on flow across sorbents chemically bonded to a rigid substrate. Although many innovations would benefit capture of CO_2 from both air and flue gas, some may be specific to capture from air.

Chapter 4 summarizes the report's findings.

Three associated topics are beyond the scope of this report. First, biological and other alternative methods of CO_2 removal from the air are not discussed in any depth. Rather, the report, focusing on only the DAC alternative, is intended to encourage emulation in reports that explore other alternatives. Second, little space given to CO_2 storage, the other half of "carbon dioxide capture and storage" (CCS), on the grounds that CO_2 storage options would not be significantly different if CO_2 were captured from a power plant or from air. The omission of CO_2 storage from this report should in no way suggest to the reader that the technologies, infrastructure and regulations required for permanent CO_2 storage are in hand. On the contrary, CO_2 storage is not yet known to be commercially feasible at the scale required to enable DAC—or for that matter, CO_2 capture from power plants—to contribute significantly to the mitigation of climate change. At least a decade of large-scale field demonstrations of CO_2 storage will be required before the long-term costs of geological disposal of CO_2 can be well estimated. Third, the report does not investigate roles for synthetic fuels derived from CO_2 captured from air in a world where substitutes for petroleum-derived fuels are strongly desired; the report nearly exclusively focuses on a world where the primary reason for considering CO_2 capture from air is to address climate change.

Only articles published before June 1, 2010, were considered.

The final version of the report, dated June 1, 2011, differs from the pre-publication version posted on the APS website in the following way: footnote 18 was added regarding commercial packing.

The report and the American Physical Society

The scope of this study was sharpened through early discussions within the Energy and Environment Committee of POPA, and the project proposal was authorized by a unanimous vote of POPA on October 3, 2008. The study was then endorsed by the Executive Board of the APS on November 15, 2008. The President of the APS conducted a peer review. The Executive Board voted unanimously to approve the report on April 28, 2011.

Acknowledgments

Chapter 1: CO_2 Removal from Air: Generic Considerations

1.1 Global climate change and CO_2 management

1.2 The physical scale of the generic sorption-desorption system

1.3 Energy and net carbon

1.4 Siting issues

1.5 Alternative strategies for CO_2 removal from air

1.6 Cost-dependent roles for direct air capture

This chapter provides context for the removal of CO_2 from air by chemical means. Section 1.1 places air capture in the context of climate change. Section 1.2 discusses physical dimensions associated with air capture systems of various scales. Section 1.3 introduces the concept of net CO_2 removal from the atmosphere, a key issue since one can expect the energy sources used to capture CO_2 to generate their own CO_2 emissions. Section 1.4 discusses site-dependent environmental issues, including below-ground CO_2 storage capacity. Section 1.5 provides a typology within which CO_2 capture with chemicals is one of several routes to CO_2 removal from air and then briefly discusses a few of them, notably biology-based options. Section 1.6 concludes the chapter by providing a context for thinking about costs.

1.1 Global climate change and CO_2 management

CO_2 in the atmosphere

Today's atmospheric concentration of carbon dioxide is about 390 parts per million by volume (ppm). This means that 390 out of every million molecules in the air you are breathing as you read this are CO_2 molecules. The current overall quantity of CO_2 in the atmosphere is 3000 billion metric tons (3000 $GtCO_2$). In this report "ton" is always understood to be a metric ton, symbol t, equal to 1000 kg. The concentration of CO_2 and its total amount are proportional: every part per million corresponds to 7.8 Gt of CO_2. Both units are important and useful.[1]

Ice cores tell us that the CO_2 concentration today is higher than at any time in the past 800,000 years. The preindustrial level was approximately 280 ppm, or 2200 $GtCO_2$. Here, "preindustrial" is understood to indicate a period of at least one thousand years prior to the year 1800, during which ice-core data show that variations in CO_2 concentration

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1   The two units are not exactly proportional. Adding a mole of CO_2 to the atmosphere changes both the numerator and the denominator in the ratio, moles of CO_2/moles of atmosphere, that defines the CO_2 concentration(ppm). Each successive new mole of CO_2 in the atmosphere has a slightly smaller effect on the ppm increase. However, since only one in 2500 air molecules is CO_2, this nonlinearity can be ignored except in much more precise calculations than those in this report.

around a central value of about 280 ppm were small. In the coldest depths of the earth's six one-hundred-thousand-year-long ice-age cycles sampled by ice cores, a characteristic CO_2 level was 180 ppm (1400 $GtCO_2$). Thus, human emissions of CO_2 in the past 200 years, in raising the CO_2 concentration from 280 ppm to 380 ppm, have produced as large an increase of atmospheric CO_2 as occurred over the roughly 10,000 years of emergence from the last ice age.

The burning of fossil fuels today releases CO_2 into the atmosphere at a rate of approximately 30 $GtCO_2$/yr, and tropical deforestation adds roughly another 4 $GtCO_2$/yr [1]. The rate of climb of the CO_2 quantity in the atmosphere is less than half as fast, thanks to the presence of strong ocean and terrestrial CO_2 sinks. The result of emissions and sinks is an increase in the atmospheric CO_2 concentration today that averages about 15 $GtCO_2$ per year (2 ppm per year, one-half percent per year).

The greenhouse effect and other greenhouse gases

CO_2 is the most important of several gases that contribute to the greenhouse effect by absorbing outgoing radiation at infrared wavelengths and reemitting some of it downward, thereby raising the average temperature of the surface of the earth. The rapidly rising concentrations of these gases are a matter of concern because they lead to unprecedented changes in climate. The additional downward radiation resulting from an increase in the concentration of all greenhouse gases other than water vapor is quantified through the concept of "radiative forcing." The anthropogenic forcing produced by any gas is the additional downward energy flux relative to the flux due to that gas in pre-industrial times. The downward flux is measured at the top of the troposphere. Water vapor, however, is accounted for differently, because additional water vapor produces not only increases in downward radiation but also changes in clouds, ice, and vegetation, some of which produce warming and others cooling [2]. The effects of water vapor are embedded in estimates of the feedbacks that amplify the total forcing from the other gases.

Today's total radiative forcing due to all greenhouse gases is approximately 2.6 W/m^2, where it is understood that this energy flux is averaged over the surface of the earth and over a year. Associated with any total anthropogenic forcing is a "CO_2-equivalent" concentration (CO_{2e}), which is the concentration of CO_2 alone that would have the same forcing as the CO_2 in the atmosphere plus additions to the atmosphere of the other greenhouse gases since pre-industrial times. Today's CO_{2e} concentration is about 470 ppm, and the corresponding CO_{2e} mass is about 3.6 trillion tons (3600 $GtCO_2$).

Of the 2.6 W/m^2 of total anthropogenic greenhouse-gas forcing, CO_2 alone is responsible for 1.7 W/m^2 and four other gases are responsible for nearly all of the rest. In descending order of contribution to total forcing, the four gases are methane (CH_4), nitrous oxide (N_2O), CFC-12 (CCl_2F_2), and CFC-11 (CCl_3F). The concentrations of methane and nitrous oxide continue to climb. CFC-12 and CFC-11 (CFC is an abbreviation of "chlorofluorocarbon") are the principal gases that have been removing ozone from the stratosphere. Thanks to international agreements their emissions have nearly ceased, but their concentrations are falling very slowly because both have lifetimes in the atmosphere of about 100 years. Many other gases contribute small amounts to the total greenhouse effect.

This report does not discuss ways of removing greenhouse gases other than CO_2 from the atmosphere. But, indeed, the instantaneous climate benefit from reducing the world's total forcing by a given amount (measured in W/m^2) is the same no matter which greenhouse gas concentration has been lowered. However, the long-term benefit of the same instantaneous reduction differs across gases, because some gases have longer atmospheric lifetimes than others.

For example, CH_4, which is oxidized in the troposphere by hydroxyl radicals (OH·) [3], has a residence time of 15-20 years, much less than the residence time of CO_2, which (oversimplified) is many hundreds of years. Thus, reducing instantaneous atmospheric forcing by the same amount through CO_2 removal provides a greater long-term benefit than through CH_4 removal.[2]

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2   Comparisons of changes in concentrations of greenhouse gases are often weighted using "global warming potentials." These compare the time-integrated forcing of any greenhouse gas to CO_2, on a per-ton basis, and they also consider a specific time period for the integration. For example, the 100-year global warming potential of CH_4 is 25, which means that the time-integrated forcing of a ton of methane added to the atmosphere today will be 25 times greater than the time-integrated forcing of a ton of CO_2, when the integration is for 100 years. Because a much smaller fraction of CH_4 than CO_2 remains in the atmosphere for 100 years (the nominal "lifetime" of CH_4 is 12 years), the GWP for CH_4 is higher than 25 for a shorter time horizon; specifically, the 20-year GWP for CH_4 is 72.

Negative emissions

Suppose the world were someday to decide that it wished to reduce the atmospheric CO$_2$ concentration by a deliberate carbon dioxide removal (CDR) strategy. Air capture by chemicals, the subject of this report, is one of several potential CDR strategies, and it is helpful to have a reference goal for a planned reduction of the global CO$_2$ concentration against which any specific CDR strategy can be assessed. In this report, in order to work with a specific example, the world is assumed to seek to reduce the CO$_2$ concentration by 50 ppm, or, equivalently, to reduce the CO$_2$ content of the atmosphere by about 400 GtCO$_2$, or by about one–eighth of its current value. Further, the goal is to achieve that reduction over 100 years by a removal at a rate that averages 4 GtCO$_2$/yr.

In one limiting case, all emissions of CO$_2$ cease, and CDR strategies are implemented to reduce atmospheric CO$_2$. Even in this case, it is not straightforward to estimate how much CO$_2$ must be removed from the atmosphere to lower its content by 4 GtCO$_2$ annually. During any period of zero emissions but no CDR implementation, the atmospheric CO$_2$ concentration will fall. Ocean currents continually bring deep ocean water to the surface that was last at the surface hundreds of years before, when the atmospheric CO$_2$ concentration was at its preindustrial value. As equilibrium is established at the ocean surface between CO$_2$ in the air and dissolved in the ocean, such ocean water scavenges CO$_2$ from the atmosphere. So, with a time scale of hundreds of years, some atmospheric CO$_2$ reduction is done for us (at the expense of growing acidity in the ocean).[3]

The same requirement for equilibrium at the ocean surface governs the reverse effect that would happen if the CO$_2$ concentration of the atmosphere were lowered someday by deliberate removal of CO$_2$. There would be an immediate compensating transfer of CO$_2$ from the ocean to the atmosphere, as a result of which it would be necessary to remove more than one unit of CO$_2$ from the atmosphere to reduce the atmospheric CO$_2$ content by one unit. Forest responses add complications, and so do deep ocean currents. Today, the combined effect of ocean and land CO$_2$ "sinks" results, for a time-scale measured in decades, in roughly half of the CO$_2$ remaining in the atmosphere that was emitted to the atmosphere by the burning of fossil fuel. The future magnitudes of these sinks are uncertain. Accordingly, for simplicity, in the rough calculations later in this report a carbon-neutral land and a carbon-neutral ocean are assumed, thereby establishing a reference case for removal of CO$_2$ from air where an average of 4 GtCO$_2$/yr is removed for 100 years.

The reference DAC system considered in Chapter 2 removes CO$_2$ from the atmosphere at a rate of 1 MtCO$_2$/yr.[4] Assuming that once installed each DAC system can be maintained indefinitely and that installation of new removal facilities occurs at a constant pace, an average removal rate of 4 GtCO$_2$/yr over a century corresponds to an installation rate of 80 MtCO$_2$/yr capture capacity each year, or 80 of these reference (1 MtCO$_2$/yr) DAC systems every year. This reference case is shown in the top panel of Figure 1.1.

After 50 years, 4 GtCO$_2$ are being removed from the atmosphere. The first 50 years of the reference case are shaded in Figure 1.1a in order to identify that this rate and scale of implementation of a mitigation strategy corresponds to one "stabilization wedge" [4-6].[5]

Building on the parameters of the reference case for CO$_2$ removal for the purposes of climate mitigation, one can see why CDR strategies are considered "slow," not at all matched to the task of reacting quickly to a climate emergency [7]. Suppose, for example, that scientists were to discover a strongly positive feedback in the climate system that could greatly accelerate surface warming. Suppose they believed that the necessary compensating response was the equivalent of removing half of the atmosphere's CO$_2$ in 10 years. Imagine, further, that at the time of the emergency, the atmosphere's CO$_2$ concentration was roughly 50% higher than today's, so that their goal, quantitatively, amounted to lowering the CO$_2$ concentration of the atmosphere from 600 to 300 ppm and doing the job in 10 years.

Such an enterprise would require an average rate of CDR of 30 ppm per year, or about 240 GtCO$_2$/yr, 60 times faster than the average removal rate for the reference case above (six times as much CO$_2$ reduction, ten times faster). Every year over the decade allowed for crisis response, 48 GtCO$_2$ of new CDR-removal capacity would need to be installed; this pace is 600 times faster than the pace in reference case. (See Figure 1.1, panel b) By comparison, imagine changing the world fleet of fossil fuel power plants in a hurry. Such plants today emit 12 GtCO$_2$/yr. The crisis response rate is

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3   Even after a period of a few thousand years of equilibration, during which CO$_2$ emitted to the atmosphere is partitioned between the atmosphere and the entire ocean, some of the CO$_2$ emissions are still in the atmosphere.

4   An important distinction between gross and net CO$_2$ removal is explored in Section 1.3 but neglected here.

5   The full 100-year triangle in Figure 1.1, panel (a), might be called a superwedge

equivalent to decarbonizing the world's fleet of power plants in just three months! For no combination of the air capture systems under consideration is such a strategy even remotely credible. For the particular case of a system involving CO_2 capture from air by chemicals followed by storage below ground, the rates of construction of facilities above and below ground are almost surely out of reach. The demand for construction materials, chemicals, and labor could be as large as or larger than the entire global market. To find "fast" strategies that conceivably could be used to respond to a climate emergency, one must look elsewhere. As briefly discussed in Section 1.5, "fast" strategies might conceivably be based on solar radiation management.
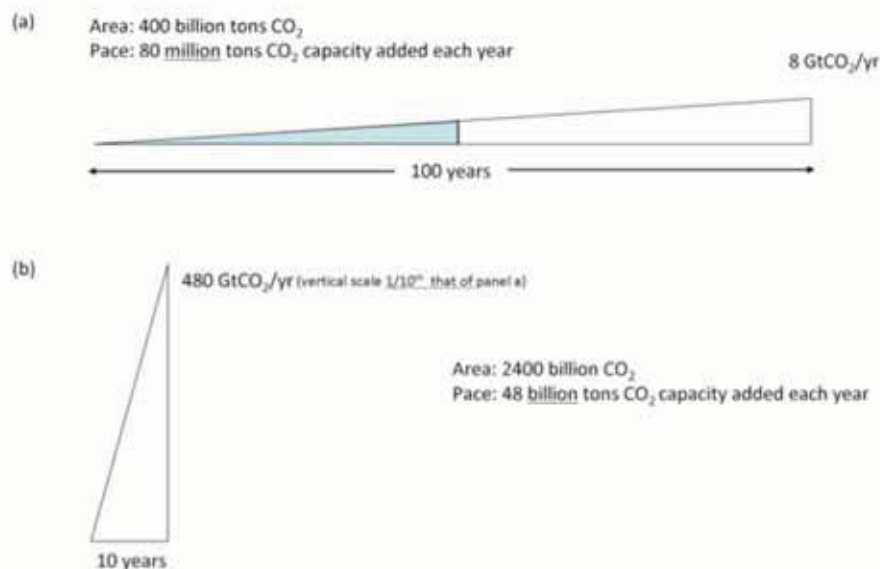
Figure 1.1.
Two CO_2 removal strategies: In (a), in 100 years the atmosphere's CO_2 concentration is lowered by 50 ppm, corresponding to a total removal of about 400 $GtCO_2$; this is the reference case for CO_2 removal in this report. In (b), the reduction—intended to represent a response to a crisis—is 300 ppm (about 2400 $GtCO_2$) in 10 years. The land and ocean are assumed to be CO_2-neutral. The "pace" is the slope of the triangle. The shaded area in panel (a) corresponds to one "stabilization wedge" (see text). The scale in panel b is 1/10th that of panel a.

1.2 The physical scale of the generic sorption-desorption system

Although several strategies to remove CO_2 from air are considered later in this chapter, this report is about one specific version, a chemical strategy involving a cycle of CO_2 sorption and desorption. In the first step, dilute CO_2 flows through a contactor and encounters a chemical to which it binds. CO_2 is released in concentrated form and the chemical is regenerated in the second step. What quantitative physical features of such a system are required to accomplish a given task?

One can start with a simple calculation, introducing reference parameters. Suppose that air flows through a contactor at two meters per second and the contactor removes 50% of the CO_2 passing through it. Figure 1.2A shows a square meter of intake area of the contactor for this case. Every cubic meter of air at atmospheric pressure and 25°C contains about 41 moles of gas. As 0.04% of this is CO_2, whose molecular weight is 44 g/mol, one cubic meter of air contains about 0.72 grams of CO_2.[6] Therefore, each second, 1.44 grams of CO_2 will pass through each square meter of the contactor and 0.72 grams will be removed. That is about 20 tons of CO_2 per year (the per capita rate of CO_2 emissions today in the U.S.).

A reference scale for a CO_2 capture plant is 1 $MtCO_2$/yr. This is the scale of the first full scale demonstrations of CO_2 capture and storage built in the past decade [8] and is matched to commercial-scale CO_2 pipelines and injection wells. Smaller facilities would confront diseconomies of small scale for CO_2 compression, transport, and storage. A 500 MW combined cycle natural gas plant, in the absence of CCS, will emit about 1.5 $MtCO_2$/yr, and a 500 MW supercritical coal plant will emit at twice that rate, so this is also the scale of single-power-plant capture. It is also the scale of the first large CCS demonstration projects that have been built around natural gas scrubbing of CO_2 (see Chapter 2).

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6   A shortcut to this result uses Avogadro's hypothesis, taught in chemistry courses: one mole of any ideal gas at 1 atmosphere and 0°C occupies 22.4 liters. At these conditions the dry atmosphere is closely approximated by a mixture of ideal gases. Multiplying 22.4 liters by the factor 298/273 takes into account an absolute temperature of 25°C rather than 0°C. Thus, 1 mole of dry atmosphere at 25°C occupies 24.5 liters.
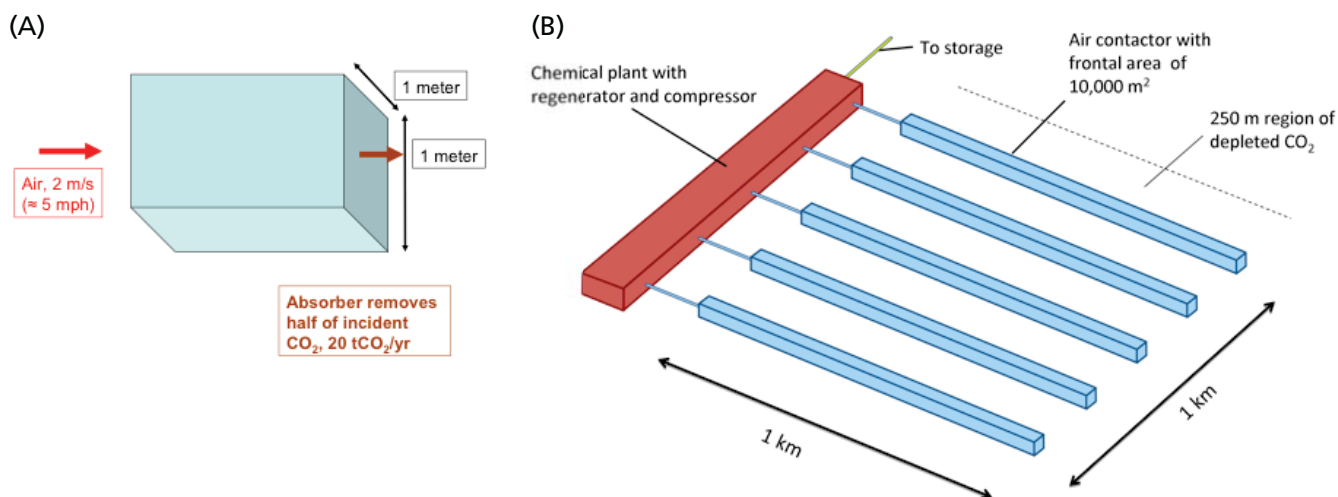
Figure 1.2. Schematic representations of A) a 1 m^2 intake area contactor capturing 20 tCO$_2$/yr, and B) a facility for capturing 1 MtCO$_2$/yr. The facility in B consists of five structures, each 10 meters high and 1 km long, and could collect 1 MtCO$_2$/yr if air passed through at 2 m/s and 50% of the CO$_2$ were collected. The structures are spaced 250 meters apart, and the footprint of the system is roughly 1.5 km^2. Approximately six of these systems would be required to compensate for the emissions of a 1 GW coal plant. Buildings not to scale.

To remove 1 MtCO$_2$/yr from the atmosphere using absorbers that remove 20 tCO$_2$/yr from each square meter of frontal area, a facility with a total area of 50,000 m^2 facing the incoming air would be required. Figure 1.2B is a schematic view of a five-contactor facility matched to this task. Each contactor is 10 meters high and 1 km long. The structures are spaced 250 meters apart so that the air exiting each contactor that is depleted in CO$_2$ can be largely replenished ahead of the next contactor. The footprint shown is 1.5 km^2, allowing for a zone of depleted CO$_2$ behind the final contactor and a central collection complex for sorbent regeneration and CO$_2$ compression. Approximately six of these systems would be required to compensate for the emissions of a 1 GW coal plant.

What about the depth of any generic air capture facility in the direction of air flow? This design variable has not been needed to make the introductory calculations above, but it is critical. If the air velocity through the contactor is held constant at 2 m/s, the depth of the contactor determines the residence time of the air moving through it; a contactor 2 meters deep would produce a one-second residence time. Longer residence time translates into greater contact with the contactor's active chemicals (sorbents), but also less yearly production per unit volume of plant.

Thus, three parameters will appear many times in this report: the air velocity, the depth of the contactor, and the percent of CO$_2$ captured.

In Chapter 2 two specific examples will be considered: *post-combustion capture* (PCC) from coal flue gas, choosing a concentration of 12% in specific calculations[7], and *direct capture from air* (DAC) at 0.04% concentration. The concentration ratio of 300 means that to bring one cubic meter of CO$_2$ through a contactor requires an input volume 300 times larger for an air capture system than for a coal flue gas (aside from adjustments for moderate differences in temperature and pressure). The factor of 300 has practical consequences regarding what can and cannot be done under plausible economic constraints.

Industry today often plans for the capture of ~90% of the CO$_2$ from the input flue gas, because marginal costs appear to decline with percent recovered until roughly this percentage is reached. The underlying reason is that many capital costs related to the collection system depend only weakly on the percent recovered [9]. The resulting CO$_2$ concentration in the output stream would then be one-tenth of 12%, or ~1.2% CO$_2$ (*~12,000ppm*), still thirty times higher than the concentration in the atmospheric *input* stream.

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7   Typical concentrations ("mole fractions") of CO$_2$ in coal power plant flue gas range from 10% to 15% and in natural gas plants range from 3% to 5%.

In some DAC systems, by contrast, strong diminishing returns might begin to occur for investments in extra collection above some more modest capture percentage than 90%. Early diminishing returns might emerge, for example, when the contactor is expensive relative to other components and is modular in the direction of air flow. If 50% of the input CO_2 is captured, the output concentration is ~0.02% (or ~200ppm) and the ratio of gas flows to capture one ton of CO_2 between the DAC and PCC systems would then be another factor of 1.8 larger, or 540.

The layout of a DAC facility consisting of several large contactors could place them end to end, but it could also place one contactor some distance behind another one. The required spacing between contactors in the direction of air flow is another important variable. The air will be depleted of CO_2 on the downstream side of a contactor for a certain distance before being replenished by mixing with undepleted air coming from the sides and top. The spacing issue for a DAC facility closely resembles the spacing issue for wind turbines on a wind farm, which need to be placed sufficiently far apart to allow most of the initial wind speed to be regained at downwind turbines.

The footprint of an air capture facility on the landscape will include much more than the structures through which the air flows. As discussed in the next section, providing the facility with electricity, thermal energy, and water produces its own demands on the land. Also, the concentrated CO_2 that is the output of the air capture plant must be placed somewhere. Today's leading candidate for long-term CO_2 disposal is the deep geological formation, accessed by a system of pipelines and injection wells.

What about a global system sized to accomplish the negative emissions task discussed in the previous section, removing 400 $GtCO_2$ from the atmosphere over a century? If all of the necessary DAC infrastructure were available immediately, the task would require the equivalent of 4000 facilities that individually capture 1 $MtCO_2$/yr and run continuously for 100 years. Because time is required for scale-up, this would be more likely achieved by gradual deployment as shown in Figure 1.1a, where 80 such facilities are constructed each year for a century, for a total of 8000 facilities—even more, when one takes into account less than continuous operation and facility turnover. Bottlenecks might emerge, involving labor, materials, logistics, and finance, but the task of building 80 of these plants each year is not hard to envision. By contrast, the task of building 48,000 plants each year for ten years as a global response to an emergency (see Figure 1.1) would create every kind of bottleneck. Among these would be limitations in the supply chain to produce the steel and other materials of construction required for the construction of very large numbers of DAC plants simultaneously.

1.3 Energy and net carbon

The energy—both heat and work—required for CO_2 capture is substantial. In a sorption-desorption system, typically, large energy demands are associated with moving the air through the contactor, but even larger energy demands are associated with the energy required to release the CO_2 and regenerate the sorbent.

In addition to the costs of the energy sources themselves, there is the net-carbon issue. Depending on how the energy is provided for any CO_2 capture system, there may be substantial associated CO_2 emissions to the atmosphere. The CO_2 removed from the air flowing through the system is called "captured CO_2" and the net change of the CO_2 in the atmosphere is called "avoided CO_2." In Chapter 2 these emissions are estimated quantitatively for a few specific systems.

For paper designs, conditions can emerge where the CO_2 emitted in association with the external energy inputs to the capture system exceed the CO_2 captured. Needless to say, such systems would not be built. A DAC system that used currently known technology would be severely compromised by high-carbon energy sources.

One way around the net carbon problem, even in a region where fossil fuels are a significant part of the energy mix, is to generate power and heat from fossil fuels at the DAC site and capture the CO_2 from these facilities. Subsequent steps would involve a unified system to transport and store the CO_2 captured from both the power plants and the DAC system. Another approach would use a nominally fully decarbonized baseload energy source—for example, a nuclear power plant, a geothermal plant, or a solar-thermal power plant with associated hydropower storage.

Even when all the energy required for air capture, thermal as well as electric, is provided by low-carbon energy sources, comprehensive accounting will produce a large difference between the gross and net quantities of CO_2 removed from the atmosphere. This is because, unless the larger regional energy system is fully decarbonized, one must consider whether an alternative use of this low-carbon energy elsewhere would have resulted in a reduction of

regional CO$_2$ emissions. If so, the carbon intensity of the entire regional system would be a more appropriate measure to use in determining the net CO$_2$ emissions associated with the energy inputs to the DAC system[8].

Because air capture is capital-intensive, it is generally assumed that every DAC facility must operate full-time. In particular, an intermittent non-carbon energy source, like solar electric power or wind, would be poorly matched to DAC unless energy storage systems were included to produce baseload power. A partial exception has been proposed by Lackner [10], where the energy to move the air through the contactor (a fraction of the total energy requirement) would be provided by the wind, and the air capture system would operate only when wind velocity exceeded some cut-in value and was less than some cut-out value. Analogous rules govern the operation of wind turbines, where annually averaged wind power is typically one-third of peak wind power. A system driven by wind must operate not only intermittently but with a very low pressure drop through the contactor.[9]

1.4 Siting issues

The siting of a DAC facility is flexible, in that CO$_2$ captured at any location has the same climate impact. Siting can be close to low-cost energy sources or favorable CO$_2$ disposal sites, for example. Nonetheless, siting is constrained by geography.

One can assume that it would be prohibitively expensive to cool or heat or dry or moisten or remove trace gases from the huge quantities of incoming air characteristic of direct air capture systems. As a result, ambient environmental conditions can be expected to affect DAC performance far more than PCC performance. Are the preferred locations for the deployment of specific DAC concepts cold or warm places, dry or humid ones, calm or windy ones? How debilitating will be the variability of these parameters, which, in many locations around the world, can vary over large ranges during the course of a year or even a day? The answers depend critically on the specifics of the DAC technology,

The water vapor in outdoor air substantially constrains system design. In outdoor air at 25°C and 50% relative humidity, there are almost 40 water molecules for every CO$_2$ molecule (a much higher ratio than in flue gas). Water vapor can compete with CO$_2$ for the reactive sites on sorbents, degrading capture performance. Water vapor can add to the thermal mass of a sorption system that must be heated during regeneration, adding to operating costs.

Other constituents of air can also create difficulties for DAC systems. The oxygen in air can react with a sorbent and shorten its commercial lifetime. Contaminants can erode surfaces and plug narrow passages in the contactor.

The variability of key environmental parameters may affect the performance of a DAC system even more than their annually averaged values. Their variability can affect the capacity factor of a DAC system—the fraction of time operating at full capacity required to produce its actual annual output. A lower capacity factor raises capture costs. Certain regions may be favorable because they exhibit relative seasonal and diurnal stability (for example, parts of the tropics).

During operation, a DAC system produces an output of air depleted in CO$_2$ that can affect downstream vegetation. Other detrimental downstream impacts would result if highly reactive chemicals are used in the sorption/desorption cycles and then evaporate into the output gas or are physically entrained in it.

The difficulties associated with the storage segment of the DAC strategy must not be underestimated. Research by governments and industry is underway to learn how to inject CO$_2$ into storage formations efficiently and to keep it out of the atmosphere for centuries. CO$_2$ storage has been commercialized to date only in conjunction with oilfield development, where the CO$_2$ commands a price. However, the storage capacity associated with oil production falls well short of what is required to have a substantial impact on climate change. The commercialization of CO$_2$ storage for climate purposes will require the use of non-hydrocarbon-bearing porous formations (saline aquifers) as well as a regulatory framework where there are specific financial rewards for storage itself.

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8   A still better measure would be the carbon intensity of the marginal energy supply that could have been displaced.

9   Assuming an air density of 1.2 kg/m³, air moving at 13 m/s (roughly, 30 mph) has a stagnation pressure of 100 Pa, the reference pressure drop through an air capture device that is used in several calculations in this report and that represents a very demanding constraint. Air moving at 26 m/s (roughly, 60 mph) has a stagnation pressure drop of 400 Pa, since the stagnation pressure varies with the square of the wind velocity. Another wind-driven system, using a Ca(OH)$_2$ sorbent, is considered by Elliot et al. [11]

Greater understanding of the supply curve for storage capacity as a function of the price paid for putting CO_2 away will be developed as field experience and regulatory policy interact. At the moment, the most nearly authoritative estimate of global aquifer-storage capacity comes from the Special Report on CO_2 Capture and Storage of the Intergovernmental Panel on Climate Change [12]: "Worldwide, it is virtually certain that there is 200 $GtCO_2$ of geological storage capacity and likely that there is at least about 2000 $GtCO_2$." Recall that the climate strategy above, reducing the atmospheric concentration by 50 ppm, requires sequestering 400 $GtCO_2$. If DAC were to be deployed after the decarbonization of centralized energy, and if a substantial fraction of this decarbonization were to be achieved via CO_2 capture and storage at facilities that burn fossil fuels (rather than via non-carbon energy sources), a storage-space constraint on DAC could arise. On the other hand, the flexibility inherent in DAC siting could weaken this constraint.

The same IPCC report also comments on the geography of industrial sources and geological sinks for CO_2: "There is potentially good correlation between major sources and prospective sedimentary basins, with many sources lying either directly above, or within reasonable distances (*less than 300 km*) from areas with potential for geological storage." Presumably, given the flexibility of siting of DAC facilities and the desirability of reducing CO_2 transport costs, most DAC facilities would be sited much closer to storage locations than 300 km.

Storage in geological formations is not the only option. An alternative storage strategy is mineral carbonation, where a concentrated stream of CO_2 is fixed as carbonate through reaction with natural silicates (very abundant on earth) or alkaline industrial residues [12-16]. An alternative to storage of any kind is to recycle captured CO_2 by reaction with hydrogen to produce liquid fuels and chemicals [17, 18]. For example, the Fischer-Tropsch reaction can be used to produce naphtha for chemical production and jet/diesel fuels. Another option would be to produce methanol for the chemical market or use it for the synthesis of olefins, aromatics, or gasoline. The fuels and/or chemicals may reemit CO_2 upon use, but can replace crude oil or natural gas derived products.

1.5 Alternative strategies for CO_2 removal from air

The Royal Society typology Direct air capture by chemicals is one of several approaches that might be used someday to remove CO_2 from the air. A recent report of the Royal Society developed a typology of carbon dioxide removal (CDR) strategies and compared them in terms of scalability, risk, pace of introduction, and cost.

Terrestrial biological CDR The Royal Society distinguishes capture on land from capture in the ocean and identifies two "biological" terrestrial CDR strategies. Both of these strategies build on the cycle that starts when green plants pull CO_2 from the air by photosynthesis. The cycle is closed when the carbon incorporated in plant tissue returns as CO_2 to the atmosphere as the plant matter is oxidized and decays. In the first strategy, which the Royal Society calls "afforestation and land use," the objective is to increase the standing stock of biomass. In the second, called "biomass/fuels with carbon sequestration," the objective is to arrange for the oxidation to occur in an engineered energy conversion facility, so that the energy released during oxidation can be put to use while the CO_2 released during oxidation is captured.

The goal of "afforestation and land use" is to increase the stock of terrestrial biomass on the land. The stock can be increased either by more dense plantings or by adding ecologically inert biocarbon (e.g., charcoal) to the soil. This strategy is arguably already underway in situations where deliberate actions to plant trees on a large scale are in force and climate mitigation is one of its explicit purposes. The most feasible route to an increase in the stock of global biomass is probably to increase the stock of biomass in forests. For each hectare of reforested land, about 500 tCO_2 can be extracted from the atmosphere as newly planted trees (perhaps several species in succession) grow to maturity [4]. The ultimate extraction of CO_2 per hectare is similar in magnitude for temperate and tropical forests, although tropical forests will typically grow twice as fast for half as long a period. The biomass in the forest planted at a single time will increase at a steadily decreasing rate until it reaches a plateau characteristic of a fully mature forest[10].

Afforestation brings many environmental benefits in addition to CO_2 removal from the atmosphere. The list includes water management and purification, habitat for wildlife, and protection of biodiversity. But it is very land-intensive. Assuming that a century is long enough for a hectare of new forest to remove 500 tCO_2 from the atmosphere, 800 million hectares of new forest will be required to reduce the atmospheric concentration by 400 billion tons, or 50 ppm,

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10   The underlying simple model is $dC/dt = S—C(t)/R$, with $C(t)$ being the forest biomass in year t, S being a constant rate of removal of CO_2 from the atmosphere as a result of constant forest growth, and R being a fixed decay time. The parameters for tropical afforestation are $S = 10 tCO_2/yr$ and $R = 50$ years; for temperate forests S is half as large but R is twice as long, so the product RxS is unchanged.

the reference CO_2 removal quantity for climate management (see Figure 1.1). This is an addition of more than a third to currently forested area (about 1500 million hectares of tropical forest and 700 million hectares of temperate forest).

Reducing the rate of deforestation could also be considered a CO_2 removal strategy associated with "land use," because deforestation reduces the stock of global biomass. Today, tropical deforestation is shrinking forest land area by roughly 30 million hectares per year [19] and introducing CO_2 into the atmosphere at a rate of about 4 $GtCO_2$, one eighth of the rate (30 $GtCO_2$ per year) at which CO_2 is being emitted to the atmosphere globally via the burning of fossil fuels.

The second of the terrestrial biological strategies is biomass energy conversion in association with carbon sequestration. The Royal Society calls this Biological Energy with Carbon Storage, or BECS. An example of BECS is fueling a power plant with an "energy crop" like eucalyptus or sugar cane that grows quickly on a dedicated plantation, to capture the CO_2 produced at the facility, and to sequester the CO_2 deep underground. There are two CO_2 capture events: an initial CO_2 capture via photosynthesis and a second CO_2 capture at the conversion facility. The net result can be that most of the CO_2 removed from the atmosphere by the energy crop during photosynthesis ends up below ground. At the same time useful heat, power, fuels, and synthetic gas for chemicals and fertilizer are produced without fossil fuels. Fast-growing energy crops can remove an order of magnitude more CO_2 from the atmosphere per hectare each year than the slow-growing trees that are best suited for building up large stocks of standing biomass over a century, substantially reducing land requirements for equivalent quantities of CDR.

A variant of BECS involves the co-firing of biomass with coal in a power plant or fuel production plant and the sequestration of the CO_2 produced from both fuels. For low fractions of biomass in the input fuel, modifications of the coal plant can be modest. For higher fractions, the result can be carbon-negative fuel and power. BECS on its own, BECS linked with coal, and direct air capture with chemicals all require the successful commercialization of geological CO_2 storage. Indeed, CO_2 captured via all three strategies would compete for the same storage space. By contrast, CDR via afforestation achieves its own carbon sequestration in the standing trees.

DAC requires inputs of energy, but BECS produces energy. As for carbon, a complete accounting for any CDR strategy requires taking into account the CO_2 emissions associated with the energy used to capture and store the CO_2. Net-carbon accounting for DAC was discussed earlier. Net-carbon accounting for both of the biological CDR strategies just considered requires taking into account the CO_2 releases associated with the energy used to plant, fertilize, and harvest the biomass (perhaps, to irrigate it as well), and in the case of BECS, additional energy used during energy conversion and CO_2 storage. Also required for carbon accounting for the biological strategies are the "indirect" CO_2 emissions—those associated with "leakage" of a land use from one location on the planet to another. For example, indirect CO_2 emissions would be included in the accounting for a biofuel produced from an energy crop, if that crop were produced on a parcel of land that previously grew soybeans, and as a result a forest was cleared somewhere else to grow soybeans to meet the same soybean demand [20-23].

A terrestrial biological CO_2 capture strategy sharing features of both biomass build-up and BECS involves "biochar." Biochar is the solid residue (charcoal) of the burning of biomass in low-oxygen conditions (pyrolysis). When added to the land, it creates long-lived soil organic carbon, enhances many soil properties and resists decay for hundreds of years. Useful energy can be extracted from the combustible gases released during the production of the biochar, as in the production of coke, the analogous product made from coal. In both cases, energy conversion from a solid fuel is terminated midway, with roughly half of the extractable useful energy still present in the biochar/charcoal.

Many questions remain regarding the long-term sustainability of biomass energy strategies, including how to sustain very high yields for many decades, how to preserve forest benefits when priority is given to carbon storage, how to preserve soil quality and yield while removing nutrients, and how to protect biodiversity while introducing new species. Nevertheless, co-benefits like enhancing the habitats of wildlife and improving soil productivity are likely to lead to the pursuit of terrestrial biological strategies well ahead of DAC—even aside from considerations of cost.

Terrestrial chemical CDR Another CDR method involves the acceleration of weathering. As a set of natural chemical processes, weathering removes CO_2 from the atmosphere on a multi-thousand-year time scale. The slow chemical processes by which certain minerals remove CO_2 from the atmosphere are exothermic and produce other minerals. (For example, minerals embedding magnesium oxide, like olivine, combine with CO_2 to make minerals embedding magnesium carbonate). Natural weathering scrubs the atmosphere of CO_2 at a rate that roughly balances additions to the atmosphere from volcanic eruptions and seeps. An accelerated weathering strategy would arrange for the same chemical reactions to occur rapidly and in a self-sustained manner [16, 24]. In one strategy, crushed olivine would be spread over agricultural or forest soils [7, 25].

Ocean-based CDR The ocean-based strategies discussed by the Royal Society include CDR via ocean fertilization. This strategy seeks to enhance the ocean's natural "biological pump," by which organisms at the ocean surface remove CO$_2$ from the atmosphere, then sink, and release CO$_2$ at depth. Local enhancement has been demonstrated for short periods of time, but it is not clear whether, globally, there will be net CO$_2$ removal when CO$_2$ is removed locally at fertilization sites [26, 27]. A second group of ocean-based strategies enhance the sea's capacity to absorb CO$_2$ by adding alkaline components derived from limestone (CaCO$_3$) or soda ash (Na$_2$CO$_3$) or by electrochemically removing hydrochloric acid from seawater [28-31].

Solar radiation management In the Royal Society typology, CDR is one of two branches. The other branch is solar radiation management (SRM).The distinction between the two categories is grounded in physics. The energy balance at the earth's surface is affected by 1) how quickly the planet is heated as a result of solar radiation absorbed on the way in from the sun, and 2) how quickly the planet cools off by emitting infrared radiation that finds its way out to space. Both can be manipulated. The subject of this report is an example of the manipulation of outgoing infrared radiation by carbon dioxide removal (CDR), which makes sending heat to space more efficient and makes the earth's surface cooler. The earth's surface can also be made cooler by solar radiation management (SRM), via an increase in the fraction of incoming solar radiation immediately reflected to space, rather than absorbed in the atmosphere or on the earth's surface. One example of SRM involves injecting water vapor into clouds at certain heights in ways that make them more reflective; another involves injecting sunlight-reflecting particles into the stratosphere [32].

The Royal Society identifies important contrasts between CDR strategies and SRM strategies. In summary, SRM can be deployed quickly and, therefore, in contrast to CDR, someday may provide an effective response to certain kinds of rapidly developing climate surprises. SRM strategies could become much less expensive than many CDR strategies that would slow climate change by the equivalent amount. However, although SRM strategies compensate for a physical property of CO$_2$, (absorption of outward infrared radiation, affecting climate), they have no impact on the chemical property of CO$_2$ whereby, upon dissolving in the ocean, it increases the ocean's acidity. Also, relative to CDR, the environmental risks of every form of SRM may be larger, and they are poorly understood. Accordingly, substantial R&D on SRM would need to be conducted before SRM could become an available option. However, an R&D program on SRM strategies would need to be conducted at a scale large enough to yield deep understanding of undesirable environmental outcomes of full deployment, yet small enough that the research itself carries no significant risk of producing the same bad outcomes. By contrast, there are no equivalent obstacles to research on CDR.

1.6 Cost-dependent roles for Direct Air Capture

In Chapter 2 the cost of one DAC option is developed in detail, and in Chapter 3 the underlying science that may permit cost reductions over time is elaborated. The broader context for that exercise is presented here.

The lower of two estimates for the cost of the version of DAC estimated in Chapter 2 is $600/tCO$_2$. Table 1.1 shows the addition to the price of primary energy (natural gas, oil, and coal) and secondary energy (gasoline, electricity from coal, and electricity from natural gas) of imposing a surcharge of that magnitude. The cost impacts are far beyond any contemplated for the next few decades, but they are characteristic of the costs later in the century in some economic optimization models.[11]

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11   From Table 1.1 and current costs one can consider the surcharge as a fraction of the price with no surcharge. This fraction is smaller for natural gas and oil than for coal. The fraction is smaller for secondary energy than primary energy, because secondary energy includes costs of energy conversion. It is smaller when related to retail costs than to wholesale costs.

Table 1.1. Effect of Adding $600/t$CO_2$ to Fuel and Power Prices

Form of Energy	Increment from $600/t$CO_2$ cost
Natural gas	$33/1000scf
Crude oil	$260/barrel
Coal	$1400/U.S. ton
Gasoline	$5.20/gallon
Electricity from coal	48¢/kWh
Electricity from natural gas	21¢/kWh

"Indirect" CO_2 emissions associated with production, transport or transmission, and distribution are not included.
Note: $600/t$CO_2$ = $2200/tC. Natural gas units: scf is a standard cubic foot, Nm^3 is a normal cubic meter.

INPUTS
Natural gas: 1 Nm^3 = 37.24 scf; 0.549 kgC/ Nm^3 natural gas
Crude oil: 1 bbl = 42 U.S. gals; 1 m^3 = 264.2 U.S. gals, 730 kgC/m^3 crude oil
Coal: 1 U.S. ton = 907 kg; 0.71 kgC/kg coal
Gasoline: 1 m^3 = 264.2 U.S. gals; 630 kgC/m^3 gasoline.
Coal power: 29.3 GJ/metric ton coal (12,600 Btu/pound); 40% conversion efficiency
Natural-gas power: 55.6 GJ/metric ton natural gas; 0.75 kgC/kg natural gas; 50% conversion efficiency

The reality is that neither DAC costs nor the costs of alternatives are known well today: much depends on the progress of future technology, environmental impacts, and public acceptance. Nonetheless, based on what is known today about DAC, its likely future costs drive forceful qualitative conclusions about the future competitiveness of DAC in three domains:

DAC is a coherent element of global CO_2 management only after the nearly all of world's remaining centralized fossil-fuel facilities are capturing their CO_2 emissions;

DAC could have some role in compensating for distributed emissions, specifically those that are not well matched to electrification or low-carbon fuels;

DAC's principal role may be to reduce the atmospheric CO_2 concentration, jointly with other CDR strategies.

A. Centralized Uses of Fossil Fuels*: Direct air capture will not become less expensive than capture of CO_2 from the concentrated streams found in power-plant flue gas and elsewhere in industry.*

CO_2 concentration is not the only important difference between flue gas and air from the perspective of CO_2 capture; in some situations DAC may benefit from a lower intake temperature, fewer contaminants, and closer proximity to storage sites. Nonetheless, there is hardly any possibility that air capture costs could fall to the point where it becomes cheaper overall to vent CO_2 from a large stationary facility and to capture CO_2 from air at a separate facility, than to capture the CO_2 at the centralized facility, at least to the 90% level, and probably to an even higher level[12]. Although some currently unforeseen advances may specifically help DAC and thereby reduce the concentration penalty, others are likely to benefit both DAC and PCC.

Removal of CO_2 from flue gas (with storage of the CO_2) is one of many ways by which the current fleet of fossil fuel power plants could be decarbonized. There are other CO_2 capture strategies (pre-combustion capture, capture after burning in oxygen), supply-substitution strategies (renewables, nuclear power), and end-use efficiency strategies that reduce electricity demand. Most of these decarbonization strategies are expected to be either less expensive than capture from flue gas or comparable in cost. Accordingly, deploying DAC to compensate for the emissions of a fossil fuel power plant that vents its CO_2 will be more expensive than many other ways of decarbonizing centralized electric power.

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12   The factor-of-300 difference in concentration of CO_2 in coal flue gas versus air means that even when 99% of CO_2 is removed from the exhaust of a coal power plant, the concentration of CO_2 in the effluent is three times more concentrated in CO_2 than in the atmosphere.

*B. **Distributed Uses of Fossil Fuels***: As a strategy to compensate for decentralized CO$_2$ emissions, such as emissions from buildings and vehicles*, DAC would compete with two important alternative paths to decarbonization: 1) using low-carbon electricity to substitute for distributed fuel use, and 2) substituting low-carbon fuels, biologically derived or produced in some other way. The extent to which DAC would be the CO$_2$-removal strategy of choice to compensate for decentralized emissions would also depend on how well it competes with other CO$_2$ removal options.*

Today, about 50% of global CO$_2$ emissions arise from decentralized energy uses in vehicles, buildings, and small industrial facilities. (About 40% of the emissions are associated with power plants and 10% with other centralized facilities.) Although sharp reductions in decentralized emissions can be expected in the face of a forceful and persistent effort to address climate change, no one knows the extent to which emissions associated with decentralized energy conversion will disappear. The price point to which the cost of a CO$_2$ removal strategy must fall to become cheaper than some strategy to decarbonize a specific distributed use of fossil fuels cannot be known today, because there are many alternative routes to decarbonization and several alternative carbon dioxide removal strategies [7].

Consider the automobile. Each dollar-per-ton of CO$_2$ charge for CO$_2$ emissions is equivalent to a surcharge of about one cent per gallon of gasoline. (See Table 1.1, and allow approximately for indirect emissions.). Thus, a transportation decarbonization strategy that incurs costs of up to about six dollars per gallon is economically viable at a CO$_2$ price of $600/ton CO$_2$. Such a price may be sufficient to increase the fuel efficiency of a vehicle dramatically and decarbonize its energy source via sustainable biofuel, sustainable hydrogen, or electrification of the vehicle and decarbonized electricity.

The prospects for decarbonization of decentralized CO$_2$ emissions face many uncertainties. Some CO$_2$ emissions from fossil fuel sources will persist as a result of the difficulty of removing the last few percent of emissions from any category of activity. Decentralized emissions may persist as a result of limitations on the future performance of batteries and fuel cells and limitations on the quantities of low-carbon fuel available. Some nominally non-carbon alternatives may not be completely carbon-neutral; an example might be a biofuel derived from an energy crop grown on a fertilized field, with fossil fuel inputs to the fertilizer. Also, institutional factors may impede decarbonization. For example, in many countries, the decentralized uses of natural gas for space and water heating in buildings and factories are located at the downstream end of a largely amortized transmission and distribution infrastructure. The sunk costs of this infrastructure could complicate replacement of gas-using devices emitting CO$_2$ locally, even in the face of low-carbon electricity-driven alternatives and high carbon taxes. The fuel infrastructure for transport may have similar recalcitrant features.[13]

*C. **Reduction of Atmospheric** CO$_2$ **Concentration**: DAC could play a role in reducing the concentration of CO$_2$ in the atmosphere. In this instance, what will matter is the extent of the desired effort and the price points and associated technical and environmental risks and benefits associated with alternative approaches to manipulating the carbon cycle, including afforestation and reforestation, biopower with CO$_2$ capture and storage, enhanced oceanic CO$_2$ uptake, and enhanced weathering.*

Direct air capture offers the potential to reduce the concentration of CO$_2$ in the atmosphere, provided that it is sustained over many decades and provided that it is accompanied by a successful system for storing the needed flux and quantity of carbon at scale and for the needed time period. A global consensus might emerge someday that anthropogenic emissions had driven atmospheric CO$_2$ concentrations to levels that were unsafe. If DAC and other strategies for removing CO$_2$ from the air were then available, they could be deployed. Gradually, but more quickly and to a greater extent than could be achieved solely by natural processes, the CO$_2$ concentration would fall. The relative roles of these strategies cannot now be assessed, because it requires a more thorough understanding of future costs for DAC and very large scale CO$_2$ storage, as well as the costs of alternative CDR strategies, also at very large scale.

The future costs of DAC and other CO$_2$ removal strategies affect the attractiveness of any "overshoot trajectories" in economic models of the world's cost-effective response to climate change. An overshoot trajectory is one where the atmosphere's CO$_2$ concentration rises above its intended stabilization target and then approaches that target from above. To take overshoot trajectories seriously today requires deciding that the risks of exceeding a stabilization target—even temporarily—are acceptable and that at least some CDR strategies will be affordable and available at scale decades from now, when, it is further assumed, the world will be much richer. The latter part of an overshoot requires a sustained period of negative global CO$_2$ emissions, which can only be achieved by the vigorous deployment of deliberate CO$_2$ removal strategies. Given the large uncertainties in the future cost of DAC and other CO$_2$ removal

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13　For an example where very high costs arise as complete decarbonization is approached, see the McKinsey analysis for the transportation sector of Germany at: http://www.mckinsey.com/clientservice/ccsi/pdf/costs_and_potentials_of_geenhouse_gas_full_report.pdf, p. 41.

strategies, century-scale economic models of global CO$_2$ emissions that feature "overshoot trajectories" should be viewed with extreme caution.

Experience suggests that the high costs estimated here using methodology used in industry may well be underestimates. Cost estimates in industry are almost always higher after the completion of pilot plant operations than when the principal guide to the estimate is laboratory results. Among the reasons for this escalation in estimated cost is the realization of the necessity for compromises in materials choices, process conditions, component efficiencies, and component lifetimes.

For nearly every new technology, the initial cost estimates developed in industry, as well as the costs actually delivered in projects, are higher than initial cost estimates found in academic, government, and consultant studies. One could say that two different questions are being answered. The published literature generally focuses on plausible costs— the costs that might result if the many foreseeable uncertainties turn out not to add substantially to total costs. By contrast, industry estimates strive for actual costs of complete facilities, estimates that capture the institutional experience of those who have actually built large, complicated facilities, where foreseeable uncertainties generally do have a big impact on actual costs. Experience suggests that actual costs are considerably higher than plausible costs.

To be sure, costs do fall when fundamentally new ideas are introduced. Chapter 3 identifies areas where progress could be achieved.

Key Messages

- Direct capture of CO$_2$ from the air by chemicals, the subject of this report, is one of a small number of ways by which the world might someday achieve "negative emissions" and, thereby, reduce the atmospheric CO$_2$ concentration.

- Two other negative emissions strategies are widely discussed: 1) adding to the planetary stock of plant life, and 2) turning plant life into electricity and fuels while capturing and storing the byproduct CO$_2$. These biology-based strategies are dramatically different from capture by chemicals and therefore comparisons are difficult, but if reducing the atmospheric CO$_2$ concentration someday becomes a global societal objective, one should expect broad parallel deployment of CO$_2$ removal strategies.

- All air capture strategies could at best act slowly (consider here is the example of 10% to 15% reduction in the CO$_2$ content of the atmosphere over a century) and therefore are not at all matched to the task of reacting quickly to an abrupt climate emergency. Even for such a slow task, air capture by chemicals requires the processing of huge volumes of air and the handling of correspondingly huge volumes of concentrated CO$_2$ after separation.

- To know the future cost of chemical direct air capture relatively well, no matter how high it is, will raise the level of understanding of low-carbon futures.

- Direct air capture will not become less expensive than capture of CO$_2$ from concentrated streams. Thus, a cost-effective deployment would be preceded by nearly complete decarbonization of all major point-source emissions, such as power plants.

- DAC could have a role as a strategy for compensating for distributed emissions from transportation and buildings, but it would need to outperform end-use efficiency, zero-carbon electricity, and zero-carbon fuel. Specifically, CO$_2$ removal strategies may be needed to decarbonize the more recalcitrant distributed uses and to eliminate the residual emissions from zero-energy strategies.

- The requirement of significant positive *net* CO_2 removal from the atmosphere will constrain DAC systems to operate with low-carbon energy sources.

- System design will be strongly affected by local environmental operating conditions (temperature, humidity, wind, and pollution content) and their variability.

- The footprint of an air capture facility on the landscape will include not only the structures through which the air flows over reactive chemicals, but also the sites providing electricity, thermal energy, and water. The footprint will be further enlarged by storage infrastructure—in the case of storage sites in deep geological formations, by pipelines and injection wells.

- Placing trust in any "overshoot" strategy for the CO_2 concentration is not wise, given the uncertainties in future costs of CO_2 removal strategies.

Chapter 2: Sorption-Desorption Systems: Technology and Economics

2.1 Generic chemical considerations

2.2 Capture of CO_2 from coal flue gas using monoethanolamine (MEA)

2.3 Capture of CO_2 from air using sodium hydroxide

2.4 Cost comparisons

In preparation for Chapter 3, where the research frontier is discussed, Section 2.1 explains a few generic chemical issues for sorption-desorption cycles that remove CO_2 from a gas mixture. In Section 2.2, the reader is introduced to a methodology used by industry to evaluate the costs of technologies when they are at an early stage of investigation. To provide a reference standard for benchmarking purposes, this methodology is used to estimate the cost of a particular CO_2 capture system nearly commercialized today for coal power plant flue gas. This background permits consideration, in Section 2.3, of one conceptual air capture system in detail.

Over the past few years other designs for DAC systems have appeared in articles and presentations (for a review see Keith et al., 2010 [33]). The particular system chosen here is based on absorption of CO_2 in a NaOH solution and its regeneration with a high temperature CaOH/NaOH cycle in use in the paper industry [34-41].

The DAC system analyzed in this chapter allows a preliminary technical and economic analysis because many of its components are similar to ones in commercial operation today, though some are still unproven. Some alternative systems for air capture that are in the early experimental or proposal stage are addressed in Chapter 3.

2.1 Generic chemical considerations

The removal of CO_2 from a gas mixture containing other chemical species is not a new challenge for chemical engineers or industry. The most prominent commercial example today occurs in the natural gas industry, where CO_2-rich natural gas must be cleansed of most of its CO_2 before it is permitted to enter the natural gas pipeline system. A typical arrangement for such a commercial CO_2-removal system is described in Box 2.1.

Gas mixtures may be separated by several technologies, including among others absorption (preferential dissolution of a species into a liquid) and adsorption (preferential adherence of a species onto a solid). In both cases, there is a thermodynamic equilibrium relationship between the concentration of species in the gas mixture and the concentration of the same species absorbed into the liquid or adsorbed onto the solid, which is a function of temperature and the interactions between the species and the sorbent. If the conditions are such that the concentration of a species in a gas mixture is greater than what would be in equilibrium with the current species concentration in the liquid or on the solid, then more species will be transferred from the gas mixture to the sorbent phase. If the conditions are the opposite, such that the concentration in the gas phase is less than what would be in equilibrium with the species concentration in the liquid or on the solid, then the species will be stripped or desorbed out of the sorbent phase.

Box 2.1 Removal of CO_2 from Natural Gas

In many locations around the world, natural gas comes out of the ground containing more CO_2 than is legally permitted in the natural gas pipeline system. To be pipeline-ready and saleable, natural gas is required to have a minimum energy content per unit volume (e.g. BTUs per cubic foot), and CO_2 may need to be removed to raise the energy content enough to meet this specification.

The signature feature of the specialized facility built to remove excess CO_2 from a gas mixture is a pair of tall cylindrical towers, as seen in the figure below (Figure 2.B1.1). In the first tower, the CO_2-rich natural gas (typically >5% or >50.000 ppm CO_2) flows upward through a high-surface-area packed material, while an aqueous solution containing CO_2-reactive chemicals (e.g. monoethanolamine (MEA) and/or other amines) flows down the surface against the gas flow. By the time the gas has reached the top of this absorber tower, ~0.3% or ~3000 ppm CO_2 remains in the natural gas, which is now suitable for pipeline transit.

In order to recover the expensive CO_2-reactive chemical in the aqueous solution, the now CO_2-rich solvent is then pumped to the top of a second regeneration tower. As the solvent flows down this tower, it is heated with steam to a high enough temperature to cause the thermal separation of CO_2 from the MEA. By the time the solvent reaches the bottom, nearly all the CO_2 has been released from the MEA solution, which is then pumped to the top of the first tower to repeat the cycle.

The CO_2 released from the solvent bubbles to the top of the regenerator and is generally vented to the atmosphere. However, in three well-known cases—at the In Salah gas field in Algeria, at the Sleipner gas field offshore Norway, and at the Snøhvit project in the Barents Sea—the CO_2 is captured and sequestered underground.

Figure 2.B1.1. Capture of the CO_2 contaminating natural gas, In Salah gas field, Algeria.

Images copyright BP, p.l.c.

At In Salah, Algeria, natural gas purification by CO_2 removal plus CO_2 pressurization for nearby injection

Separation at amine contactor towers

A basic two-step sequence used for CO_2 capture from a gas mixture then involves the interaction in a suitable *contactor* of a CO_2-rich gas with a *sorbent* containing molecules that have affinity for CO_2 and physically or chemically bind to it, followed by the separate *desorption* or *regeneration* under different conditions that releases the CO_2 from the sorbent. The same two-step sequence is likely to be the common core of most systems designed to capture CO_2 from the flue gas of a coal or natural gas power plant or from the air. Important operational considerations include the nature of the interaction between the species and the sorbent, the temperature, and how low a residual concentration of the species in the sorbent can be obtained.

Figure 2.1 shows a generic systems diagram for any CO_2 capture system. Sorption and regeneration are embedded within a network of material and energy fluxes required to fulfill the energy (heat and work) and water requirements.

An important design choice is the reactive sorbent used to bind the CO_2. This choice influences the rate at which CO_2 is removed from the processed gas and also the energy needed to regenerate the sorbent and release the CO_2. Strategies to compensate for the lower concentration of CO_2 in air could be to operate at lower temperatures, employ sorbents that have been stripped to extremely low residual concentrations of CO_2, or to choose chemicals that bind CO_2 more strongly than those used to extract CO_2 from flue gas. However, regeneration from strongly binding sorbents can require so much energy as to render the entire system unworkable. Chapter 3 identifies the need for sorbents whose performance improves the current trade-off between reactivity and regeneration energy as one of the most important research challenges for both post-combustion capture (PCC) and direct air capture (DAC).
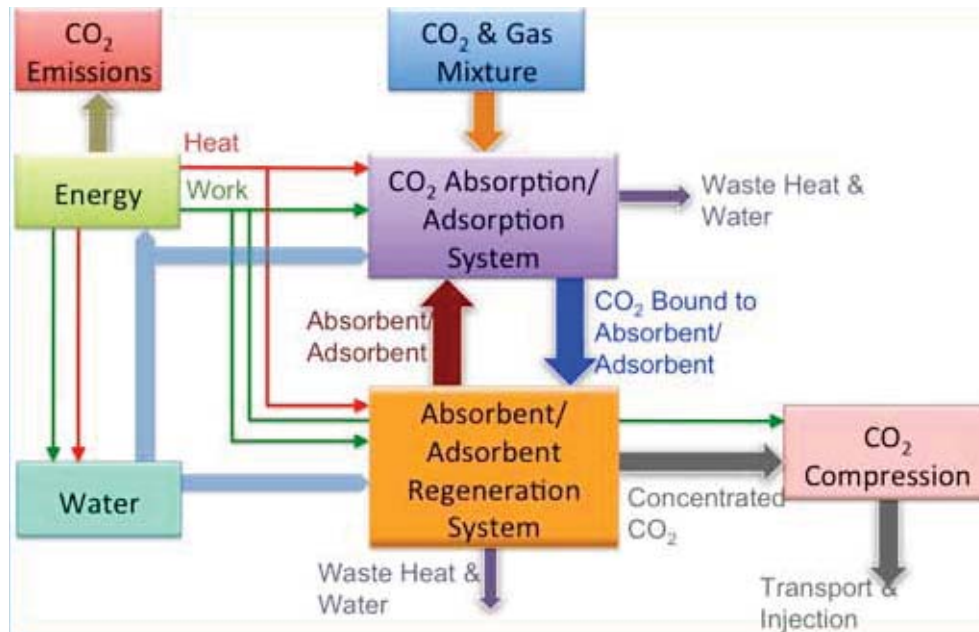
Figure 2.1 A typical system for CO_2 capture. One key component is a CO_2 absorption/adsorption system where CO_2 is chemically bound to another molecule, and removed from the gas mixture. The other key component is an adsorbent/absorbent regeneration system where CO_2 is released in a concentrated form, which is then compressed. These processes require energy (heat and work) and water. Work is in the form of electrical or mechanical power.

Energy inputs

Thermodynamics provides a point of reference for any separation of one gas from another gas when they are initially mixed together. Oversimplifying, there is less disorder (lower entropy) in the world when the two gases are separated than when they share a common volume, and the entropy of the world can only be decreased by the expenditure of energy. (This is the Second Law of Thermodynamics.) Thermodynamics provides the minimum amount of energy to achieve such a separation, a value that depends on the absolute temperature and the initial and final concentrations and pressures.

The details are in Box 2.2., which also graphs the theoretic minimum energy required to separate CO_2 over a wide range of initial CO_2 concentrations. The minimum energy varies logarithmically, not linearly, with the CO_2 concentration. As a result, the thermodynamic minimum energy required to remove CO_2 from a mixture where its initial concentration is 0.04% (characteristic of air) is about three times larger than the corresponding minimum energy when the initial CO_2 concentration is 12% (characteristic of coal flue gas). The minimum values are 497 kJ/kg CO_2 (21.86 kJ/mole) for 0.04% initial concentration and 172 kJ/kg CO_2 (7.58 kJ/mole) for 12% initial concentration. This energy difference provides a reason why it is preferred to capture a large fraction of the CO_2 from concentrated point sources rather then emit the CO_2 to the atmosphere for later capture.

Box 2.2 Thermodynamic Minimum Energy to Remove CO$_2$ from a Gas Mixture

Mass balances Consider *n* moles of a gas mixture at atmospheric pressure (either flue gas from a power plant or air), which contains CO$_2$ and a second inert gas, and where CO$_2$ has a mole fraction, *y*. Consider a process that captures a fraction, α, of the CO$_2$, collects it pure at atmospheric pressure, and leaves the rest of the CO$_2$ with the inert species. At the start there is one mixture, and at the end there are two mixtures, one of which is in fact pure CO$_2$. The process proceeds at constant temperature.

The laws of thermodynamics allow the calculation of the minimum work required for such a separation. This minimum work is equal to the absolute temperature of the initial and final mixtures, multiplied by the difference between the initial entropy and the final entropy of the system.

The quantities involved are constrained by material balances, which require that both the total number of moles of all gases and the total number of moles of CO$_2$ are conserved:

$$n = n_{cap} + n_{em} , \tag{1}$$

$$yn = n_{cap} + z\, n_{em} . \tag{2}$$

Here n_{cap} is the number of moles of captured CO$_2$, n_{em} is the total number of moles of the remaining gas that are emitted, and *z* is the CO$_2$ mole fraction in the emitted gas. Using the definition of the fraction captured, α, yields:

$$n_{cap} = \alpha\, y\, n \tag{3}$$

Substituting (3) into (1) and (2) one obtains:

$$n_{em} = (1 - \alpha y)n, \tag{4}$$

$$z = y(1 - \alpha)/(1 - \alpha y). \tag{5}$$

Entropy The entropy per unit mole of any gas mixture, s, is calculated relative to the entropies of the mixture components at the same conditions. It is given by the following relationship, where *x* is the mole fraction of one component, and (1 - *x*) that of the other:

$$s = -R\, [x \ln x + (1 - x)\, \ln(1 - x)]. \tag{6}$$

Here, *R* is the ideal gas constant (8.314 J/mole-K). Note that the entropy of a pure gas species is 0 with this convention, and that the entropy of a mixture is always positive. These values are consistent with the Second Law of Thermodynamics, which states that the entropy of an isolated system cannot decrease spontaneously: a mixture cannot spontaneously disassemble into pure states of its components.

The entropy change associated to the separation process described above is therefore:

$$\Delta S = sn - s_{em}\, n_{em} =$$

$$= n\, R\{(1-\alpha y)[z \ln z + (1-z)\ln (1-z)]—[y\ln y + (1-y)\ln(1-y)]\} \tag{7}$$

Here, s_{em} is the molar entropy of the final mixture that contains the CO$_2$ that is not captured. The minimum energy required for the separation, per *unit mass of CO$_2$ captured*, w_{min}, is:

$$w_{min} = T\Delta S/(M_{CO2}), \tag{8}$$

where M_{CO2} = 44 g/mol is the molar mass of CO$_2$. Note that the result does not depend on the initial number of moles, as expected.

Box 2.2, cont'd. Thermodynamic Minimum Energy to Remove CO_2 from a Gas Mixture

Table 2.B2.1. Thermodynamic minimum energy to capture CO_2 from a gas mixture (kJ/kgCO$_2$) at 298K

Fraction of CO_2 captured (α)	PCC (0.12 CO_2)	DAC (0.0004 CO_2)
1.0	172.2	496.9
0.9	158.1	482.5
0.75	147.1	470.8
0.5	134.9	457.8

Table 2.B2.1 presents these minimum energies per unit mass of CO_2 separated, for two initial concentrations and three values of α, the mole fraction of the initial CO_2 that is removed as a pure state. The two initial concentrations are 12% (typical of coal flue gas) and 0.04% (typical of air). The four values of α are 1.0, 0.9, 0.75, and 0.5.

From Table 2.B2.1, the minimum work when starting with coal flue gas at 12% CO_2 is 172 kJ/kg CO_2, and when starting with air at 0.04% CO_2 it is 497 kJ/kgCO$_2$, approximately three times greater. The corrections for less than complete separation are small: for flue gas, the minimum work is about 8% less for 90% removal, 15% less for 75% removal, and 22% less for 50% removal than for 100% removal. The corresponding fractional reductions for direct capture are 3% for 90% removal, 5% for 75% removal and 8% for 50% removal.

By comparison, the burning of a high-quality coal produces energy and CO_2 emissions in the ratio of ~11,000 kJ/kgCO$_2$[42], a ratio approximately 20 times larger than the thermodynamic minimum for air. For natural gas (using the value for methane, CH_4), the ratio of energy produced to CO_2 emitted is ~20,000 kJ/kgCO$_2$.[43]

Systems where the separated CO_2 is less than pure, subjected to a similar analysis, reveal a minimum energy requirement for capturing CO_2 that is lower, the more impure the separated CO_2. Depending on the intended disposal or recycle strategy for the captured CO_2, there are upper limits on the fractions of other gases that can be co-separated with CO_2.

Equation (7) simplifies for the condition that the captured CO_2 is pure and all of the CO_2 in the initial mixture is removed. Then $\alpha = 1, z = 0$, and the first term in square brackets in Equation (7) is zero. For 100% removal, the minimum energy per unit mass of CO_2 removed, $w_{min, all}$, is:

$$w_{min, all} = - [RT/(y\, M_{CO2})][y \ln y + (1-y)\ln(1-y)]. \tag{9}$$

There is a minus sign at the left on the right hand side of Equation (9) because the expression that follows is negative and the minimum work is positive. Figure 2.B2.1 plots this minimum energy. The minimum work increases as the mole fraction of CO_2 in the initial gas mixture decreases. Note that the Figure is consistent with the column of the Table for $\alpha = 1$.
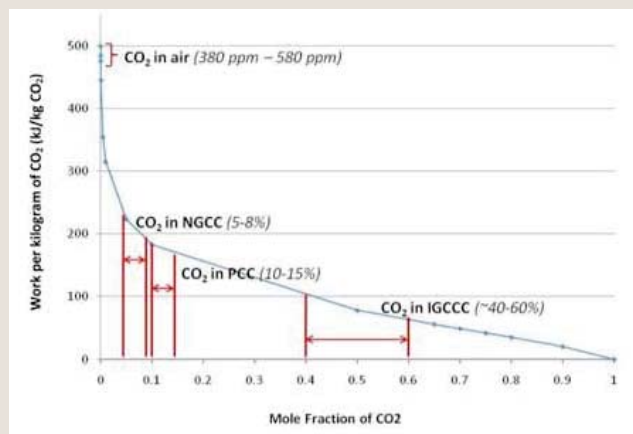
Figure 2.B2.1 Thermodynamic minimum work per kg of CO_2 separated from air vs. initial CO_2 concentration, at 25°C, for the limiting condition that in the end state all of the CO_2 is separated and pure.

In the systems studied in this chapter, the CO$_2$ is compressed after it is separated. Thermodynamics also provides a reference minimum energy for specific compression pathways. In Box 2.3, the thermodynamic minimum work for isothermal (constant-temperature) CO$_2$ compression is developed.

The thermodynamic minimum corresponds to reversible processes happening infinitely slowly and as a result would require an infinite capital investment. Moreover, energy inputs are required not only for the separation cycle but also for moving gases and liquids external to the cycle. For both reasons, in actual chemical plants energy inputs exceed the thermodynamic minimum energy by a considerable factor, but by a smaller factor when energy is a major cost component. One of the key objectives in plant engineering design is to trade capital cost against operating cost to find the minimum total cost. Chapter 3 explores prospects for chemical cycles for DAC systems that could come closer to the thermodynamic minimum than the cycles discussed in this chapter's case study. This search ultimately must occur within such an economic context.

Box 2.3 Thermodynamic Minimum Compression Energy for Isothermal Compression

To compare the estimated energy actually required for the processes in Chapter 2 with the thermodynamic minimum energy required, one needs to take into account that in the systems being studied, CO$_2$ is compressed after it is captured. Thus, to the minimum energy required to concentrate CO$_2$ discussed in Box 2.2, one must add the minimum energy to accomplish the subsequent compression.

Assume that the compression is isothermal (i.e., throughout the compression, the temperature is constant) and choose the constant temperature to be 25°C. For isothermal compression from 1 atmosphere to 10 atmospheres at that temperature, the ideal gas approximation would be adequate, and the thermodynamic minimum compression energy, $W_{min}^{compress}$ [kJ/kg] would be proportional to the logarithm of the ratio of the final pressure (P_2) and the initial pressure (P_1):

$$w_{min}^{compress} = R\,T\,ln(P_2/P_1) \,/\, (\alpha\,n\,y\,M_{CO2}), \qquad \text{(ideal gas, isothermal compression)} \qquad (1)$$

where T is the absolute temperature of the initial and final states. To compress CO$_2$ at 298 K from 1 to 10 atmospheres, using Equation (1), the minimum energy of compression is 130 kJ/kgCO$_2$, comparable to the values in Table 2.B2.1 for the minimum separation energy for flue gas.

However, in the systems of interest in Chapter 2 compression is from 1 atmosphere to 100 bar, a much higher pressure. The state of CO$_2$ exiting the compressor is near the critical point, whose pressure and temperature are 73.8 bar and 31.1^{o}C, respectively. Therefore, the ideal gas approximation is not helpful for compression to such a high pressure. However, available enthalpy and entropy tables permit the estimation of the thermodynamic minimum energy for isothermal compression:

$$w_m in^{compress} = (h_2 - h_1) - T(s_2 - s_1) \quad \text{(any isothermal compression)} \qquad (2)$$

The first term (the enthalpy term) in Equation (2) is zero for an ideal gas, but it is negative for this problem, as seen in Figure 2.B2.1; a large fraction of the enthalpy reduction occurs during the phase change, as attractive molecular forces bring the CO$_2$ into a more dense state at the same pressure. The second term (the entropy term) is also negative, because compression increases the order of the system. In fact, the second term is more negative than the first term. Tables [44, 45] show that the enthalpy difference is -249.5 kJ/kgCO$_2$ and the entropy difference is -1.568 kJ/kgCO$_2$-K. Therefore, for T = 298K (25°C), the minimum work is 217.8 kJ/kgCO$_2$. This value is used in Chapter 2 to compare actual energy expenditure with thermodynamic minimum energy required.

2.2 Post-combustion capture of CO$_2$ from coal flue gas using MEA

PCC case study: technology description

The case study of post-combustion CO$_2$ capture from a coal power plant considered in this section is based on the 90%-capture example ("Case 1") presented in a 2007 report of the National Energy Technology Laboratory (NETL), "Carbon Dioxide Capture from Existing Coal-Fired Power Plants" [9]. Table 2.1 describes the parameters of the

separation process. CO_2 capture is achieved with an amine-based system. The capacity of the plant is 434 MW before retrofit, and with an assumed 90% capacity factor the initial emissions are 3.11 $MtCO_2$/yr, or 7.2 $MtCO_2$/yr for each gigawatt of installed coal power.[14] The retrofit results in the capture of 90% of the plant's initial emissions, or 2.79 $MtCO_2$/yr. The retrofit is integrated with an existing, highly regulated power plant. Post-combustion capture at this scale has not yet been commercialized and still carries scale-up technical risk.

Table 2.1. Parameters for the NETL post-combustion capture system [9]. The energy unit, GJ_e, is billions of joules of electricity (1 GJ = 278 kWh).

Table 2.1 PCC Separation Parameters	PCC [9]	
SPECIFICATIONS		
CO_2 capture plant capacity	Mt/yr	2.8
CO_2 capture rate	%	90
CO_2 concentration in	% vol	12.8
CO_2 concentration out	% vol	1.3
Gas molecular weight	g/mol	28.6
Gas velocity	m/s	3.0
Gas temperature	°C	40
Gas pressure	bar	1
Gas density	kg/m³	1.1
Absorbent concentration	mol/L	5 (MEA)
Liquid density	kg/m³	1,050
Liquid to gas ratio	mol/mol	3.40
Pressure drop through absorber	Pa/m	170
Time on-stream	h/yr	8,000
ABSORBER		
Absorber cross-section	m²	169
Absorber depth	m	38.5
Absorber volume	m³	6,500
MATERIAL BALANCES		
Gas flow through absorber	Mm³/h	1.8
CO_2 captured	t/h	350
Liquid flow through absorber	Mt/h	0.006
ENERGY (per ton CO_2 captured)		
Absorber fans	GJ_e/tCO_2	0.033
Liquid pumping	GJ_e/tCO_2	0.0004

As seen in Figure 2.2, the process involves flows through two columns operating at different temperatures (see Box 2.1). The active chemical sorbent is an aqueous solution of monoethanolamine, "MEA" (NH_2-CH_2-CH_2-OH, molecular weight of 61). In the lower-temperature column (the "absorption column"), CO_2 is removed from the flue gas by the MEA solution. In the higher temperature column (the "stripper"), CO_2 is released. Absorption at one temperature and desorption at another temperature is an example of a "temperature swing."

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14   Elsewhere in this report the assumed CO_2 emission rate for coal power is rounded off to six $MtCO_2$/yr per GW.
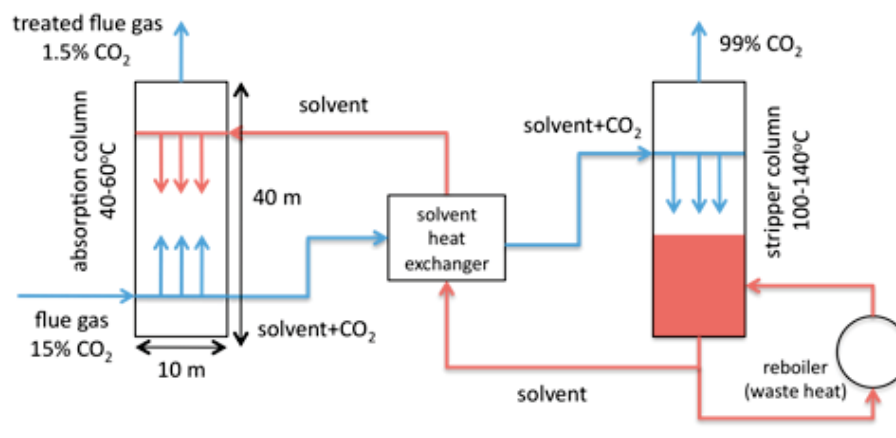
Figure 2.2 Schematic of a CO_2 absorption system used for post-combustion capture based on the report DOE/NETL-401/110907.

The process begins when flue gas is introduced into a packed absorption column about 40 meters high by 10 meters in diameter [9]. The concentrations (mole fractions) of the four principal gases in the reference flue-gas mixture entering the MEA absorber are 12.8% vol. CO_2, 68.3% nitrogen, 2.9% oxygen, 16.0% water vapor; these four constituents account for nearly all of the flue-gas mixture.

The absorption operates at 40-60°C. The aqueous amine solution flows down from the top of the column, and the flue gas flows up from the bottom. The MEA is 30% of the solution by weight (approximately 5 moles MEA per liter of solution). The treated flue gas (~1.3% vol. CO_2) exits from the top of the column, and the rich amine solution (~6 % wt. CO_2) is transferred to the stripper through a heat exchanger. The inlet temperature of the solvent entering the absorber is chosen so as to avoid net losses of water from the MEA solution and net gains of water by the solution (see Box 2.6 for a quantitative discussion of this issue in the context of DAC, whose concepts apply also to PCC).

At the stripper, which operates at 100-140°C, the CO_2 is released from the amine solution. The solution, now lean in CO_2, is transferred back to the absorption column via a heat exchanger. A small amount of MEA exits the stripper with the CO_2 and is recovered by water wash and returned to the absorber. However, some amine is also lost because at the stripper temperature it thermally degrades [46] and when exposed to oxygen in the absorber it oxidizes [47]. As a result, in the case of MEA, 0.5 to 3.0 kg must be replaced for every ton of CO_2 captured.

MEA also reacts with SO_2 and SO_3 (collectively, called "SOx") to create salts that can lead to loss of the amine absorbent. Thus, for MEA-based post-combustion capture to be successful, it should take place only after most of the SO_x compounds are removed from flue gas. Standard methods of flue-gas desulfurization to meet regulatory emissions requirements are typically not sufficient to meet MEA requirements. In standard methods a wet limestone slurry contacts the flue gas and removes 97-98% of the SO_x, but for this use of MEA the SO_x concentration must be lowered to ~10 ppm. A secondary SO_x absorber is required and is a component of the total capital cost to retrofit the power plant for CO_2 capture.

Energy inputs

All of the power and heat required for the retrofit is assumed to come from the power plant itself, including the power for CO_2 compression. The output of the plant is reduced by this additional "parasitic load" to 303 MW, i.e., by about 131 MW, or 30%. 1.03 million MWh/yr are not produced by the plant as a result of the retrofit and must be produced elsewhere. The retrofit preserves the 90% capacity factor, and the recovered CO_2 leaves the plant as a stream at ~100 atmospheres (10 MPa) pressure.

The energy requirement of the CO_2 capture system reduces the power export capacity of the plant, increases the plant's capital and operating costs, and reduces the net CO_2 additions to the atmosphere. The parasitic load reflects demands for both electricity and heat. A major component of the electricity load is required to run the compressor.[15] The heat for the absorption and stripper columns that remove and isolate the CO_2 from the flue gas and regenerate

15   From Table 2.1, the energy for pumps and fans is a very small fraction of the total parasitic power. The fan power, 0.033 GJ/tCO$_2$ * 2.79 MtCO$_2$/yr, is only 3 MW. Note that the fan power calculated in Table 2.1 is simply the product of the volumetric flow rate and the pressure drop and does not include an efficiency factor for the fans. Taking this efficiency into account does not change the qualitative conclusion.

the MEA absorbent solution generally comes from process steam extracted between the outlet of intermediate-pressure turbines and the inlet of the low-pressure turbine. Because this steam is therefore unable to go through the low pressure turbines to generate power, the thermal load also contributes to the parasitic power. The heat required for regeneration is supplied by >25% of the available plant steam and accounts for more than half of the total requirement for heat and power combined.

PCC case study: cost analysis

The NETL report [9] is the source of the purchased equipment costs and operating parameters used here to generate a high-level economic analysis that results in a cost of captured CO_2. Table 2.2 presents the results and Appendix 2A comments on the costing methodology.

Table 2.2. Cost estimates for a coal-power PCC system (Costs in $/ton CO_2 are italicized.)

	Post-Combustion Capture: Coal
CO_2 Captured (Tons per annum)	2,790,000
Capital Cost Estimate	
Purchased Equipment Cost ($ millions)	$113
Total Installed Capital Cost ($ millions)	$500
Depreciation over 20 years ($/ton CO_2 captured)	*$9*
7% Return of Investment (ROI) ($/ton CO_2 captured)	*$13*
Depreciation + ROI ($/ton CO_2 captured)	*$22*
Operating Cost	
Maintenance ($ millions per annum)	$20
Labor ($ millions per annum)	$8
Chemicals ($ millions per annum)	$12
Maintenance, Labor and Chemicals ($/ton CO_2 captured)	*$14*
Fuel Consumption (million BTU per annum)	102,000
Fuel Cost ($ per million BTU)	$6
Fuel Cost ($ millions per annum)	$1
Fuel Cost ($/ton CO_2 captured)	*$0.22*
Power Consumption (MWhr per annum)	1,030,000
Power Cost ($ per MWhr)	$71
Power Cost ($ millions per annum)	$73
Power Cost ($/ton CO_2 captured)	*$26*
Total Annual Operating Cost ($ millions)	$114
Operating Cost ($/ton CO_2 captured)	*$40*
Cost per Ton CO_2 Captured	
Capital Cost ($/ton CO_2 captured)	*$22*
Operating Cost ($/ton CO_2 captured)	*$40*
Total Cost ($/ton CO_2 captured)	***$62***
Cost per Ton CO_2 Change in Atmospheric CO_2 Content ("Avoided Cost")	
Avoided CO_2 as a fraction of CO_2 captured at the device	0.77
Capital Cost ($/ton CO_2 avoided)	*$30*
Operating Cost($/ton CO_2 avoided)	*$50*
Total Cost ($/ton CO_2 avoided)	***$80***

As explained in Appendix 2A, the first step in arriving at the total capital costs in Table 2.2 is to estimate the purchased equipment cost. The purchased equipment cost for the PCC plant is assumed to be the sum of the costs for purchasing the four major units that must be added to a conventional coal plant to enable PCC. These four units are:

- A second absorber train for the flue gas desulfurization block, to bring the SO$_x$ concentration in the flue gas below 10 ppm

- A CO$_2$ capture and regeneration system based on a 5-molar MEA solution

- An additional let-down turbine to enable the power-plant steam system to provide heat for amine regeneration and CO$_2$ release

- A CO$_2$ dehydration and compression island

The purchased major equipment cost is taken from the NETL report [9] and sums to $110 million when price adjusted to an early 2009 basis. This cost is then multiplied by 4.5 to arrive at the estimated final installed capital cost, approximately $500 million. A 20-year economic life for the plant is assumed, with 5% and 7% of total capital costs assigned to the annual value for depreciation and the return on investment, respectively. These percentages are appropriate for preliminary project screening. The resulting annualized capital cost is $60 million per year, or $22/tCO$_2$. The use of the 4.5 factor is an estimating technique used in the refining and chemical industries to convert purchased equipment cost to final installed cost. The general methodology for use of this type of multiplying factor is discussed in Appendix 2A.

The use of this multiplicative factor instead of the detailed capital costing found in the NETL report allows the use of a common tool for both the PCC case and the DAC case in the next section. While the PCC process steps have been investigated both individually as well as on an integrated basis at the pilot and demonstration plant scale, DAC steps have not. As a result, one lacks the data necessary to properly define the operations of the DAC plant. The application of the multiplicative factor is usually limited to systems such as DAC, where data are lacking. Here, it is being used for PCC as well, in order to provide a calibration for the DAC example in Section 2.3.

Operating costs associated with retrofitting the power plant to incorporate the PCC system include increased costs for maintenance and labor, the cost of replacement chemicals, and the cost of producing less power at the plant because of the parasitic power demand for the capture system. The total annual incremental operating cost for the PCC system is ~$114 million, or (dividing by the quantity of CO$_2$ captured annually) ~$40 per ton of CO$_2$ captured. The resulting "capture cost," which is the sum of the annualized capital and operating costs, is ~$62 per ton CO$_2$ captured. Note that this value does not include the cost to transport and sequester the CO$_2$. The $62/ton of CO$_2$ captured is comparable to the $59/ton of CO$_2$ captured for the 90% capture case in the NETL report [9], especially when the 2007 value of $59/ton is adjusted to a 2009 cost basis, bringing it to $61/ton.

Energy cost vs. the thermodynamic minimum

Compare the energy requirement for this PCC plant with the thermodynamic minimum value for 90% flue gas capture of 158 kJ/kg, or 158 MJ/ton developed in Box 2.2. If one adds the theoretical minimum compression power of 218 MJ/ton, or 0.069 MWh/ton (See Box 2.3), the minimum thermodynamic value becomes 376 MJ/ton. If a power output of 1.03 million MW$_e$h/yr is given up in order to capture 2.79 MtCO$_2$/yr, this is a power requirement of 0.370 MW$_e$h/tCO$_2$ or 1330 MJ$_e$/ton. (Writing MW$_e$h or MJ$_e$ with a subscript "e" emphasizes that the separation energy is provided by electricity, which is secondary energy. When there is no subscript, primary energy is being reported.) If the conversion of primary energy to electricity is 100% (an efficiency approximated at a hydropower plant), then the primary energy requirement for this PCC plant is 1330 MJ$_e$/ton, which is just three and a half times the thermodynamic minimum. If the power is from a fossil fuel power plant with only a 40% power generation efficiency, the 1330 MJ$_e$/ton secondary energy becomes 3330 MJ/ton. Therefore considering the primary energy required, the PCC plant operates at nearly nine times the thermodynamic minimum. The corresponding ratios are higher for calculations that exclude the compressor from the capture system, because modern compressors have a much higher thermodynamic efficiency than the rest of the capture system.

Net carbon and "avoided cost"

As explained above and in Box 2.4, the cost of CO_2 avoided is a more important value to consider than the cost of CO_2 captured. The 1.03 million MWh of power not produced at the plant will be produced elsewhere on the grid. If the make-up power were produced at the estimated average carbon intensity of the US power grid today, ~610 kgCO_2/MWh [48], about 0.63 MtCO_2/yr would be produced elsewhere to compensate for the parasitic power. Since the PCC retrofitted power plant captures 2.79 MtCO_2/yr, the net CO_2 emissions credited to the capture plant would be 2.16 MtCO_2/yr after deducting the emissions associated with compensating for the plant's reduced output. That is, the "avoided CO_2 emissions" are 77% of the "captured CO_2 emissions." As a result the avoided cost (cost per ton of CO_2 avoided) for this PCC retrofit is about \$80/tCO_2 (the cost per ton of CO_2 captured, \$62/tCO_2, divided by 0.77). Note that the avoided cost of \$80/tCO_2 is an underestimate, because it does not include the cost of CO_2 transport and sequestration, which depends on the specifics of sequestration route and may bring the total cost of avoided carbon dioxide to over \$100/tCO_2.

As the fossil-carbon intensity of the power grid declines over time, the quantity of avoided CO_2 emissions and the quantity of CO_2 captured will converge, and therefore the cost of CO_2 captured and the cost of CO_2 avoided will converge as well. The cost to which they converge will reflect changes in the cost of power generation as the grid decarbonizes.

Box 2.4 Gross and Net CO$_2$ Emissions at any Facility Capturing CO$_2$

In any analysis of a capture facility, both gross and net CO$_2$ emissions will be estimated. Let the gross amount of CO$_2$ captured be M$_{cap}$ [tCO$_2$]. Gross emissions are a feature of the capture facility in isolation. Net emissions are a property of the larger system and track what has happened to the atmosphere. A capture facility will be paid for net CO$_2$ reductions, assuming some explicit or implicit cost per ton for CO$_2$ emissions.

In this report two paths are taken to find net CO$_2$ emissions. In section 2.2, the case of a retrofit of a coal plant for post-combustion capture, output power capacity is reduced by the retrofit because the "parasitic power" required to operate the plant is increased and because, by convention, the separated CO$_2$ is compressed inside the plant. The power not produced by the plant because of the retrofit is assumed to be produced by an average plant on the same grid, at some carbon intensity.

In Section 2.3, the case of a facility that captures CO$_2$ from air, the carbon intensities of the external heat and work are taken into account directly. The algebra is straightforward: Let the external heat and work inputs per ton of CO$_2$ captured be Q and W [kJ/tCO$_2$ captured], respectively, and let c_q and c_w [tCO$_2$ emitted /kJ] be the corresponding carbon intensities. Thus, the product c_qQ is the tons of CO$_2$ emitted by the source of heat per ton of CO$_2$ captured, and similarly for the product c_wW with respect to the source of work. Both products are fractions. The "avoided" emissions, M$_{avo}$ [tCO$_2$], which are net CO$_2$ emissions from the point of view of the atmosphere, are:

$$M_{avo} = M_{cap}(1 - c_Q Q - c_W W) \qquad (1)$$

Total capture costs, to be sure, include the costs for heat and work. What is conventionally called "the capture cost," C_{cap} [\$/tCO$_2$], is the total capture cost divided by the total quantity of CO$_2$ captured by the facility. Accounting for associated CO$_2$ emissions for heat and power, the cost per ton of CO$_2$ *avoided*, C_{avo} [\$/tCO$_2$] is:

$$C_{avo} = \frac{C_{cap}}{1 - c_Q Q - c_W W} \qquad (2)$$

In principle M_{avo} in Equation (1) could be negative and C_{avo} in Equation (2) could pass through infinity. Such a capture system would make no sense, because the net result of attempting to restrict emissions to the atmosphere or remove CO$_2$ from the atmosphere would be to add CO$_2$ to the atmosphere! Indeed, no capture system would be designed where the denominator in Equation (2) is significantly less than one, or, equivalently, that has a much larger cost of CO$_2$ avoided than its cost of CO$_2$ captured.

Mixed-source sequestration of CO$_2$ captured from air and CO$_2$ captured from its fossil energy inputs Natural gas or coal could provide on-site power and thermal energy for an air-capture facility, and the CO$_2$ emissions from these sources could be separately captured. The subsequent steps would involve co-transport and co-storage. This option is explored in Section 2.3.

2.3 Capture of CO$_2$ from air using sodium hydroxide

DAC case study: technology description

The reference plant for this case study is based on a scheme published by Baciocchi et al.[34]. This scheme was chosen because it both relies largely existing technology and provides detailed information on material and energy balances that are necessary for a cost analysis of an industrial process.

The system operates with countercurrent flow through many squat cylindrical towers (each 2.8 m high and 12 m in diameter) and captures 1 MtCO$_2$/yr. Fans drive air through an absorption bed containing suitable packing material, and a sodium hydroxide solution flows counter-currently to the air flow. As discussed in detail below and in Box 2.5 the capture system consists of two intertwined cycles: a sodium based cycle (via sodium hydroxide and sodium carbonate) and a calcium based cycle (involving calcium carbonate, calcium oxide and calcium hydroxide) [34, 36]

Box 2.5 Sodium Hydroxide and Calcium Hydroxide Cycles for CO_2 Capture

The complete absorption and regeneration process illustrated schematically in the enthalpy diagram below involves four reactions. The vertical scale shows the relative enthalpies of four states, with the enthalpy scale set arbitrarily to zero for the initial mixture (NaOH, CO_2 and $Ca(OH)_2$), while the chemical reactions driving each transition are illustrated at each level.

The CO_2 is captured by an aqueous solution of NaOH and converted into a solution of sodium carbonate (Na_2CO_3). As shown in the Figure 2.B5.1a, step 1 is exothermic by 109.4 kJ/mol, or 105 kJ/mol including solvation energy. The Na_2CO_3 in the solution is highly soluble, which is desirable because build up (scaling) on the inside surfaces of the absorption column is avoided. However, as a result of its high solubility, the Na_2CO_3 cannot be directly precipitated out of solution without the evaporation of large quantities of water which would be too energy intensive; instead, in Step 2, it is converted to a calcium carbonate ($CaCO_3$) precipitate by adding calcium hydroxide ($Ca(OH)_2$). This step is exothermic by only 5.3 kJ/mol or 8 kJ/mole including solvation energy, but the equilibrium is driven towards $CaCO_3$ through its precipitation. Step 2 regenerates the NaOH solution for return to the absorber. In Step 3, the $CaCO_3$ precipitate is converted to CaO (quicklime) and CO_2 through calcination. This $CaCO_3$ decomposition reaction is endothermic by 179.2 kJ/mol and requires high-temperature (T > 800°C), hence high-temperature heat, to make it possible for CO_2 release at a pressure close enough to atmospheric pressure. The CO_2 is then compressed for transportation to the storage site and, in Step 4, the solid CaO is transformed into a suspension of $Ca(OH)_2$ from reaction with water in a slaker [34].
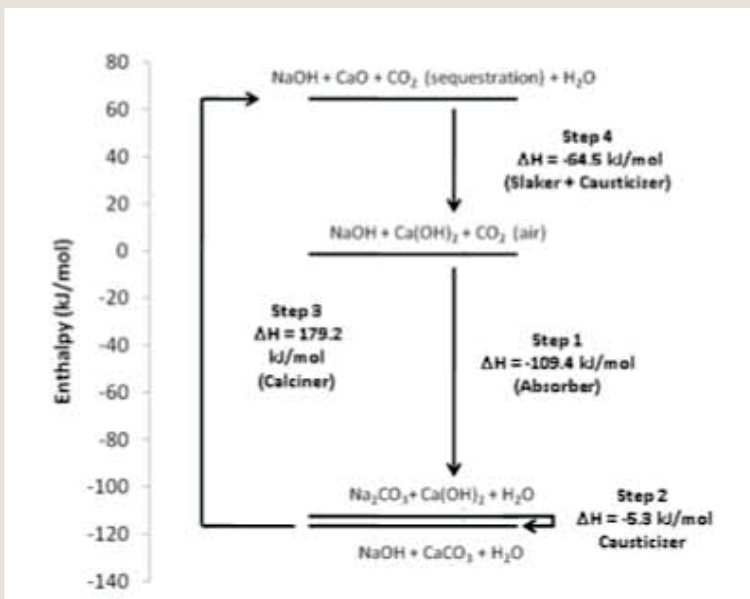
Figure 2.B5.1a. Enthalpy level diagram for CO_2 absorption and regeneration by sodium hydroxide (NaOH). Note that each level has the same set of atoms. In the system studied here, some molecules do not participate in specific physical processes; for example, ideally, NaOH is not transported to the calciner, nor does $Ca(OH)_2$ participate in the absorption.
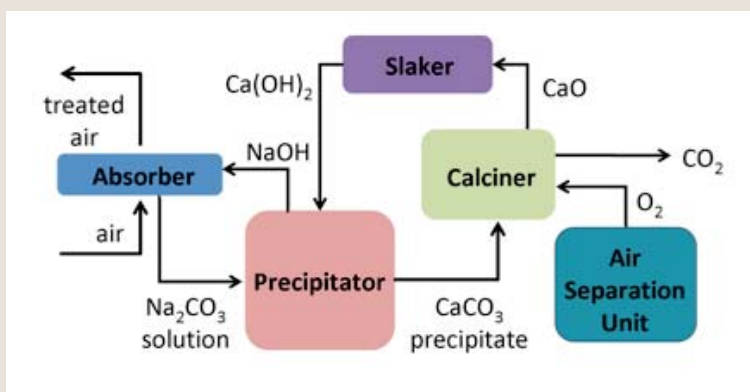
Figure 2.B5.1b. Scheme of a plant for CO_2 capture from air that uses NaOH as the absorber. The pulp and paper industry calls the reactor labeled "precipitator" a "causticizer." In this reactor, calcium carbonate is precipitated and sodium hydroxide (popularly called "caustic soda" as well as "lime") is regenerated.

As explained in Box 2.5, CO_2 is captured by contact with sodium hydroxide (NaOH) in solution to form sodium carbonate (Na_2CO_3):

2 NaOH (solution) + CO_2 $\longrightarrow$ Na_2CO_3 (solution) + H_2O,   ΔH = -105 kJ/mole
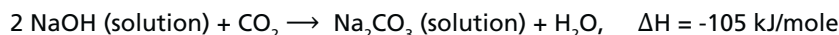
The very strong binding energy associated with this reaction provides the potential for high loadings of CO_2 over a wide range of operating conditions and system designs, but more significantly brings with it the associated disadvantage of equivalently high energy requirements for releasing the CO_2 during the regeneration stage.

Even with the highly reactive chemistry of NaOH absorption, the large volume of air that needs to interact with sodium hydroxide solution during the absorption step remains a major challenge. In order to maximize the air-solution interaction, the contactor in this design must create a large surface area for the gas and liquid to interact. The CO_2 is absorbed into the solution across the air-solution interface and reacts with the sodium hydroxide in solution. Moving air through the contactor, moving the sodium hydroxide solution, and moving other fluids around the system all require energy.

The regeneration of the sodium carbonate to release the CO_2 and restore the reactive sodium hydroxide solution is a complex challenge. While one could simply evaporate water from the absorption solution to isolate a solid containing sodium carbonate for subsequent thermal decomposition, the high energy consumption to evaporate the water would make such a process impractical. The system under consideration here accomplishes regeneration by adding a calcium hydroxide cycle to the sodium hydroxide cycle.

Regeneration begins with the addition of calcium hydroxide, $Ca(OH)_2$, to the sodium-carbonate-rich solution leaving the absorber, which results in the formation of a calcium carbonate precipitate and regenerates the sodium hydroxide solution:

Na_2CO_3 (solution) + $Ca(OH)_2$ (slurry) $\longrightarrow$ $CaCO_3$ (wet solid) + 2 NaOH (solution)   ΔH ~ -8 kJ/mole
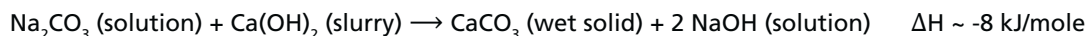
The precipitate is then heated to remove excess water using waste heat from the calciner (kiln) which is used to decompose the calcium carbonate. The calcium hydroxide is itself regenerated in two steps. First, the calcium carbonate is heated in a kiln to release the CO_2 and produce calcium oxide, CaO.

$CaCO_3$ (solid) $\longrightarrow$ CaO (solid) + CO_2 (gas)   ΔH = 179 kJ/mole
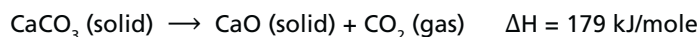
This is the most energy-intensive step, because a large energy cost is required to undo the strong binding of the CO_2. The calcium carbonate is heated to above 900°C [34] to drive the reaction toward desorption of the CO_2. Then, the calcium oxide calcination product reacts with steam in a slaker to regenerate the calcium hydroxide.

CaO (solid) + H_2O $\longrightarrow$ $Ca(OH)_2$ (slurry)   ΔH ~ -65 kJ/mole
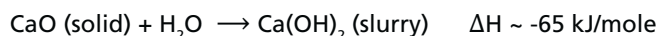
In order to promote good heat transfer and efficiency, the energy for calcium carbonate decomposition can be provided by natural gas, burned either in air or oxygen. Burning in oxygen produces high-purity CO_2 after the removal of water vapor in the effluent, but has the disadvantage that it requires an air separation unit upstream, with the associated energy penalty and cost. Moreover, such an oxygen-fired kiln has not yet been demonstrated. An alternative would be to use an air-fired kiln, but then the large volume of nitrogen in the kiln exhaust must be separated from CO_2 afterwards, in effect requiring the addition of a post-combustion capture system on the back of the calcium carbonate decomposition step. In either case, the CO_2 produced from burning the natural gas needs to be captured and co-stored with the CO_2 captured from air. In the present example, use of an oxygen-fired kiln has been assumed.

If this system were to prove technically feasible, it would demonstrate that capture of CO_2 from the atmosphere is already achievable at some cost using modifications of existing technology. Potential difficulties even at this early stage, however, include fouling of the absorber with calcium carbonate and with precipitates that result from the aerosols in the intake air, water evaporation from the sodium hydroxide solution in the absorber, and loss of sodium hydroxide solution entrained in the CO_2-depleted effluent air leaving the absorber. Learning how to deal with such practicalities and to reduce their negative impacts will require experiments in the field.

An important design variable is the concentration of the NaOH in the aqueous solution (its "molarity," moles of NaOH per liter of solution). The capture reaction is enhanced at high molarity, but the solution is also more viscous and more aggressive, hence more difficult to handle. The molarity also affects the water balance of the collector, because, together with the relative humidity and the temperature of ambient air, it determines the extent to which, during the contact of the air with the sodium hydroxide, moisture will evaporate from the solution to the air. The water loss is discussed in Box 2.6.

Box 2.6 Water Loss from an Aqueous Sodium Hydroxide Solution to Moist Air

The water loss to an air stream after contact with an aqueous sodium hydroxide solution results from the difference between the moisture content of the ambient air entering the absorber and the moisture content of the air leaving the contactor. Such quantities can be estimated using the following definitions and assumptions.

1. The moisture content of the inlet ambient air is proportional to the water partial pressure, P_{in}, which can be calculated as the product between the vapor pressure of water at the ambient temperature, T_{in}, and its relative humidity R_H, which depends on the local climate and weather conditions:

    $P_{in} = P_v(T_{in}) R_H$.

    The average relative humidity for instance in New York City is 65%, whereas in Tucson, Arizona, it is 40%

2. The moisture content of the air leaving the absorber is again proportional to the water partial pressure, P_{out}, which can be calculated as the product between the vapor pressure of water at the temperature of the air leaving the absorber, T_{out}, and its degree of saturation S, which depends on the conditions in the absorber and its operation:

    $P_{out} = P_v(T_{out}) S$.

3. The vapor pressure of water at a given temperature T can be calculated using the following equation:

    $P_v(T)=611.2 \exp(17.62\, T / (243.12+T))$

    where T must be input in °C and P_v is obtained in Pa. At 20°C the water vapor pressure is 2,330 Pa (the water vapor concentration in air at 20°C is 23,300 ppm); at 0°C it is 610 Pa; at 10°C it is 1,230 Pa; at 100°C it is 1 bar, i.e. 100,000 Pa.

4. Let us define the difference in the partial pressures of CO_2 in the inlet and outlet air streams as ΔP_{CO2}. For example, if 50% of the CO_2 is captured from ambient air, the initial CO_2 concentration of which is 500 ppm, then ΔP_{CO2} is 25 Pa, i.e. 250 ppm.

5. These definitions and a simple material balance yield the following relationship for the molar ratio between the net water loss and the CO_2 captured, $r_{H2O/CO2}$, i.e. the specific water loss:

    $r_{H2O/CO2} = (P_v(T_{out}) S - P_v(T_{in}) R_H) / \Delta P_{CO2}$ mol H_2O/mol CO_2.

    Note that since the same air flow carries both carbon dioxide and water vapor the air flow rate cancels out in the above expression. The corresponding mass ratio is obtained by using the relevant molecular masses, i.e. M_{CO2}=44 g/mol and M_{H2O}=18 g/mol:

    $R_{H2O/CO2} = M_{H2O} (P_v(T_{out}) S - P_v(T_{in}) R_H) / (M_{CO2} \Delta P_{CO2})$ mol H_2O/mol CO_2.

    When this quantity is negative, a net absorption of water vapor from ambient air occurs that causes dilution of the absorbing solution.

6. In order to estimate the specific water loss we make the following reasonable assumptions about the CO_2-lean air leaving the absorber: (i) it is at the same temperature as the incoming NaOH solution; (ii) its water vapor content is in thermodynamic equilibrium with the NaOH solution of molarity M; (iii) the presence of CO_2, carbonate and bicarbonate in the NaOH solution can be neglected.

Box 2.6 Water Loss from an Aqueous Sodium Hydroxide Solution to Moist Air, cont'd

7. The critical quantity in the equations above is the degree of saturation, S, which under the assumptions above depends only on temperature and NaOH concentration in the absorbing solution. Since the NaOH solution exhibits a strongly non-ideal thermodynamic behavior, the relation between degree of saturation and NaOH molarity is best given in graphical form, as shown in Figure 2.B6.1 for the two temperatures of 0°C and 20°C (the diagram is obtained combining data from Tables 2-29 and 2-92 of [49]). Both curves start from S=100% and are monotonically decreasing, thus indicating that the presence of NaOH in solution reduces water volatility. The upper bound along the horizontal axis is set by the maximum NaOH solubility in water, which increases with increasing temperature. The diagram shows for example, that at both temperatures a solution with M=5, i.e. 5 moles or 200 g of NaOH per liter of solution, is at equilibrium with air at a degree of saturation S=80%. Although the vapor pressure of water at 0°C is four times smaller than that at 20°C the two curves are almost exactly overlapping. Indeed, all the curves for saturation vs. NaOH concentration in the range of temperatures of interest (i.e., between the water freezing point and ambient) are one and the same.

8. One can verify that the data for the degree of saturation shown in Figure 2.B6.1 differ from what would be expected for an ideal solution, to an increasing extent as the molarity increases. If the solution behaved ideally, the value of S would be the mole fraction of water in solution. Since the addition of x moles of NaOH to 1 liter of water forms a solution containing 55.5 moles of water plus 2x moles of ions (Na+ and OH-), the degree of saturation for an ideal x-molar NaOH solution would be 55.5/(55.5+2x). The value for 10M NaOH, would be 0.735, as compared with the observed value in Figure 2.B6.1 of about 0.45.
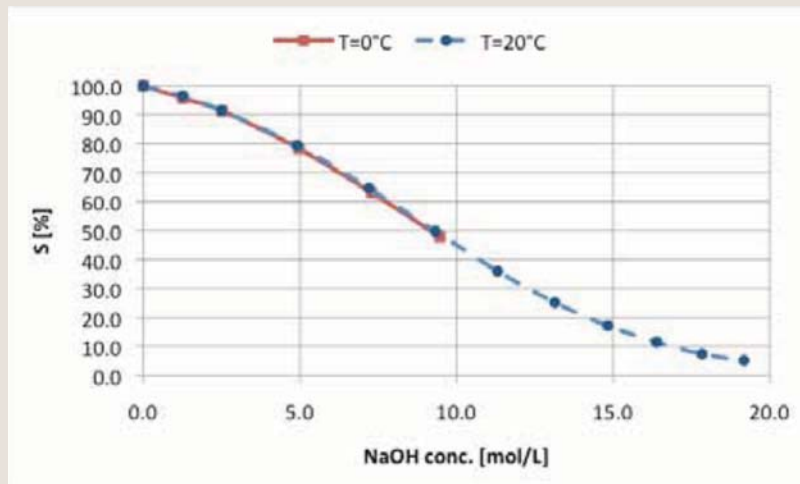
Figure 2.B6.1 Degree of saturation (equivalently, relative humidity) of air in equilibrium with a NaOH solution, as a function of the molarity of the sodium-hydroxide solution. Nearly identical curves for 0°C and 20°C show that the degree of saturation is essentially temperature-independent in the region of interest.

The equations above together with the Figure 2.B6.1 allow calculating the specific water loss at any operating condition. For example, for 50% CO_2 capture in Tucson, Arizona (R_H is 40%) using a 5 M NaOH solution (S is 80%) under conditions where both inlet and outlet temperatures are 20°C one obtains:

$$R_{H2O/CO2} = 18 \times 2,330 \ (0.8 \text{—} 0.4) \ / \ (44 \times 25) = 15 \ t \ H_2O/t \ CO_2.$$

Using a 10 M NaOH solution instead (S=45%), one would lose 1.9 t H_2O/t CO_2.

It is worth noting that optimal operation of a DAC absorber requires that the water loss calculated above be neither positive (this would add to the costs of the process) nor negative (an equivalent amount of water should be continuously evaporated lest the NaOH solution were progressively diluted). For given conditions of the ambient air, i.e. inlet temperature and relative humidity, the equations above allow determining the right combination of sodium hydroxide concentration and temperature of the absorbing solution that make the specific water loss be zero or close to zero. Considering for instance the same example as above but with a solution temperature as low as T_{out}=10°C, one would reach water losses of only 0.8 ton per ton CO_2 captured; at T_{out}=9°C, one would attain negative water losses of - 0.2 ton per ton CO_2 captured.

DAC case study: material balance and energy inputs

The PCC cost analysis in the previous section utilized data from a NETL report [9]. The costs in the NETL report were based on a detailed equipment list and process energy and material balance. However for DAC, the lack of experimental data on sorption-desorption cycles for CO_2 in air, particularly the absence of results from integrated pilot or demonstration plants, precludes the development of an integrated plant design with an energy and material balance at the level of detail of the NETL report for PCC. The uncertainties of the individual process performance parameters in any simulated system imply that the sizing of equipment and the estimates of associated energy and material balances can only be rough approximations.

As a first step toward a baseline design, this report builds on an analysis by Baciocchi et al. [34] that explores the two intertwined sodium-based and calcium-based cycles and provides simplified mass and energy balances based on existing commercial technologies. The process design for this reference system is derived from engineering design criteria as well as a number of parameter choices that in principle should be based on a detailed cost optimization but that in practice reflect engineering experience and sensitivity analysis. Among these parameters are the NaOH concentration in the absorber, the ratio between liquid and gas flow rates, and the gas velocity.

This reference system captures 1 MtCO_2/yr, which is roughly equal to the annual CO_2 emissions from a 300 MW natural gas combined-cycle power plant or a 150 MW supercritical coal power plant. Such a system is large enough to take advantage of economies of scale in CO_2 transportation and storage. The front end of this system is a contactor, consisting of many absorbers operating in parallel. The contactor's structure and internals, including piping and packing, are the largest component of the purchased equipment cost.

The reference contactor removes 50% of the CO_2 in incident ambient air that is assumed to have an initial concentration of 500 ppm CO_2.[16] Baciocchi et al. choose a cylindrical absorber of 12 m in diameter and 2.8 m in length, a 2 M NaOH solution, and a 2 m/s velocity of the air through the absorber. A side-by-side comparison of process data for the DAC and PCC absorbers is shown in Table 2.3.

The low concentration of CO_2 in the air requires the movement of large volumes of air through the absorber system, 10 billion moles of air per hour. In order to keep the pressure drop through the absorber manageable, a squat absorber design is chosen, and the absorber is operated under conditions that lead to a pressure drop of about 100 Pa/m. Given the process parameters in Table 2.3, the number of absorbers required is ~330, resulting in a total absorber cross section of 37,000 m^2. The energy requirements associated with the DAC contactor drive the air and the NaOH solution continuously through the absorbers.

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16   The concentration used elsewhere in this report is 400 ppm, close to today's value of about 390 ppm.

Table 2.3. Parameters for the NETL post-combustion capture system [9] (previously shown in Table 2.1) and the corresponding parameters for the reference air capture system [34].

Separation Parameters		PCC	DAC
SPECIFICATIONS			
CO$_2$ capture plant capacity	Mt/yr	2.8	1
CO$_2$ capture rate	%	90	50
CO$_2$ concentration in	% vol	12.8	0.050
CO$_2$ concentration out	% vol	1.3	0.025
Gas molecular weight	g/mol	28.6	28.8
Gas velocity	m/s	3.0	2.0
Gas temperature	°C	40	25
Gas pressure	bar	1	1
Gas density	Kg/m³	1.1	1.2
Absorbent concentration	mol/L	5 (MEA)	2 (NaOH)
Liquid density	Kg/m³	1,050	1,080
Liquid-to-gas mole ratio	mol/mol	3.40	1.44
Pressure drop through absorber	Pa/m	170	100
Time on-stream	h/yr	8,000	8,000
ABSORBER			
Absorber cross-section	m²	169	37,000
Absorber depth	m	38.5	2.8
Absorber volume	m³	6,500	104,000
MATERIAL BALANCES			
Gas flow through absorbers	Mm³/h	1.8	268
CO$_2$ captured	t/h	350	125
Liquid flow through absorbers	Mt/h	0.006	0.28
ENERGY (per ton CO$_2$ captured)			
Absorber fans	GJ$_e$/tCO$_2$	0.033	0.63
Liquid pumping	GJ$_e$/tCO$_2$	0.0004	0.07
Electricity subtotal (fans and pumps only)	GJ$_e$/tCO$_2$	*0.033*	*0.70*

The back end of the DAC plant involves the formation of a calcium carbonate precipitate and the subsequent decomposition of the calcium carbonate to liberate the CO$_2$. Ahead of the kiln where calcination takes place, calcium carbonate must be filtered, dried and heated to the calcination temperature. Table 2.4 presents the process parameters and material and energy balances for these steps as estimated for Case B by Baciocchi et al. Case B assumes that calcium carbonate is precipitated in a pellet reactor that permits efficient dewatering and reduces the residual moisture content in the solid pellets conveyed to the calciner to 10% wt. [34]

Table 2.4. Materials and energy balances for the recovery of CO_2 in the reference DAC scheme, case B of [34].

DAC CO_2 Recovery Parameters		DAC
SPECIFICATIONS		
Kiln temperature	°C	900
CO_2 pressure after compression	bar	100
Residual moisture in $CaCO_3$ pellets to kiln	% wt.	10
Time on-stream	h/yr	8,000
MATERIAL BALANCES		
Liquid flow to precipitator	t/h	280,000
Liquid flow from slaker	t/h	773
Pellets to kiln (90% wt. $CaCO_3$)	t/h	305
Solid CaO from kiln to slaker	t/h	154
Methane fuel to kiln	t/h	18
Oxygen from air separation unit (ASU) to kiln	t/h	81
CO_2 to storage	t/h	171
ENERGY BALANCES (per ton CO_2 captured)		
Precipitator and slaker	GJ_e/tCO_2	0.11
Air separation (ASU)	GJ_e/tCO_2	0.55
CO_2 compression	GJ_e/tCO_2	0.42
Electricity subtotal	GJ_e/tCO_2	*1.08*
$CaCO_3$ heating	GJ_t/tCO_2	2.2
$CaCO_3$ drying	GJ_t/tCO_2	0.9
$CaCO_3$ calcining	GJ_t/tCO_2	4.5
Air heating	GJ_t/tCO_2	0.8
Overall heat recovery	GJ_t/tCO_2	-2.3
Thermal energy subtotal	GJ_t/tCO_2	*6.1*

Beside the absorber, the other two main power users are the cryogenic air-separation plant providing oxygen for the kiln and the CO_2 compressor train. Oxygen firing is required for the kiln to avoid significant amounts of nitrogen in the effluent. The power demand for CO_2 compression takes into account the need to compress 0.43 tons of CO_2 produced by burning natural gas to provide heat to the calciner (see below), for each ton of CO_2 captured from the air. Combining the power demands in Tables 2.3 and 2.4, the total power requirement is 1.78 GJ_e for each ton of CO_2 captured, i.e., 0.49 MWh/tCO_2. [17]

As seen in Table 2.4, nearly all of the thermal energy requirement arises from the operations of drying and decomposing the $CaCO_3$ to release CO_2. Only the high-grade heat in the process is assumed to be recoverable, namely the heat associated with cooling the solid quicklime and the kiln's flue gases. The result is a heat recovery credit—a negative quantity in Table 2.4. The net thermal energy requirement for the DAC plant is estimated at 6.1 GJ for each ton of CO_2 captured. This energy is assumed to be provided at 75% thermal efficiency by combustion of natural gas in the oxygen-fired kiln, resulting in a total thermal energy input of 8.1GJ (7.7 million BTUs) per ton of CO_2 captured.

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17   As in Table 2.1 the fan power in Table 2.3 is the product of the volumetric flow rate and the pressure drop and does not include an efficiency factor for the fans. This simplification results in a small underestimate of the total power requirement for this DAC plant (here, the sum of the electricity subtotals in Tables 2.3 and 2.4).

DAC case study: cost analysis

In costing the DAC process design described above, one can exploit industrial experience with gas separation technologies. For the specific design under consideration here, with the mass and energy flows reported in Tables 2.3 and 2.4, an analyst using industrial costing tools can estimate the cost of building a large DAC facility today. This estimate relies on the costing methods outlined in Appendix 2A, and is reported in Table 2.5. (Table 2.5 repeats the PCC cost data in Table 2.2 and includes two extra columns for DAC costs.) By using the same costing methodology and also keeping many other features of the two systems the same (such as the final pressure to which captured CO_2 is compressed: ~100 atmospheres pressure), the ratio of the DAC and PCC cost estimates should be more robust than the cost estimates for either PCC or DAC alone. Note that the DAC cost estimated here is not the cost of an Nth generation DAC facility, because technological learning is not included. On the other hand, the proposed design for this case study involves many relatively mature technologies that have been chosen in order to reduce risk, so cost reductions for N[th] generation facilities of this kind relative to the initial units may be modest.

As with the estimate of PCC costs in the previous section, annualized capital costs and operating costs are separately developed. In general, process parameters are at the optimistic end of a realistic range of values.

Capital costs

As explained in Appendix 2A, the total capital cost is the product of the total major equipment purchase cost and a capital multiplying factor. For the DAC system, an optimistic capital cost estimate would use the multiplying factor of 4.5, the same as the factor that was used in the PCC case. Holding this factor constant simplifies comparisons. A higher multiplying factor, such as 6, could be justified to generate a potentially more realistic capital cost reflecting the novelty of the major DAC unit operations. Cost estimates for DAC below will use both factors.

The multiplying factor accounts for a wide range of construction and other costs including engineering, owner's costs, site preparation, foundations and installation, piping, tanks, control systems, buildings, utilities, start-up expenses and contingencies. It does not include the cost of land.

Assuming that 90% of the volume of each of the 330 absorbers is filled with high-performance packing, and using the total absorber volume of 104,000 m^3 from Table 2.3, each absorber requires ~285 cubic meters of packing. The bulk cost of the engineered structural packing (for example, Sulzer Mellapak 250Y [34]) is estimated to be ~$1700/$m^3$, resulting in a purchased cost of approximately half a million dollars for packing for each absorber, and a total purchased cost for packing of $160 million.[18] The total cost of the purchased equipment for the 330 contactors—including the shell, internals and packing—is estimated to be $290 million.

The estimated total cost of the major pieces of equipment required for the calcium carbonate cycle is $190 million. This is the sum of estimated purchase costs derived from recent industrial experience for four components:

- Precipitator to produce calcium carbonate from sodium carbonate, separators for the regenerated sodium hydroxide solution, and leacher to form calcium hydroxide: ~$25 million

- Calciner to decompose calcium carbonate and release CO_2: ~$120 million

- Air-separation unit to provide ~81 t/hr of oxygen for the kiln: ~$15 million

- Compressor to produce "sequestration ready" CO_2 (at 100 atm) : ~$31 million

The total purchased equipment cost is thus ~$480 million, of which ~60% comes from the air contactors. Applying the multiplicative factor of 4.5, a total capital cost estimate is just under ~$2.2 billion for a DAC system capturing one million tons of CO_2 per year. Using the same economic factors for capital depreciation (5% of capital) and return on investment (7% of capital) as were used for the PCC plant (see Appendix 2A), the annualized capital cost is ~$260 million per year, or ~$260 per ton CO_2 captured. Using the higher 6.0 multiplicative factor, the total capital cost estimate is ~$2.9 billion, with translates to a higher annualized capital cost of ~$350 million per year.

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18   The operating physical packing parameters used here are taken from Reference 34. In that reference, Mellapak 500Y was the selected packing, based on performance specifications available at that time. After updating the performance specifications and applying a unit-conversion correction to the Reference 34 operating parameters, Mellapak 250Y emerges as having operating physical parameters more nearly resembling those used in this report. As for packing cost, which has a substantial impact on total cost, it can be expected to fall with volume of production.

Operating costs

The total operating cost is built up from estimates of both variable and fixed costs as in post-combustion capture. The sum of the costs for maintenance, labor, and chemicals is ~$90 million per year, or ~$90 per ton of CO_2 captured.

As to the energy costs, we assume for the sake of comparison that power is supplied by the power grid at the same cost, $71/MWh, as in the PCC case. Therefore, at a power requirement of 0.49 MWh/tCO_2 the cost of power is ~$35 per ton of CO_2 captured, or ~$35 million per year.

Furthermore, assuming a natural gas cost of $6 per million BTU delivered to the DAC plant and considering the heat requirement of 7.7 millions BTUs per ton of CO_2 captured, the cost of thermal energy is ~$46 per ton of CO_2 captured, or ~$46 million per year .

As a result, the total operating cost for energy (power and heat) is ~$80 per ton of CO_2 captured. There is also a small operating cost for chemicals that takes into account expected physical losses of sodium and calcium hydroxide during separations as well as chemical reactions with contaminants in the air, such NOx and SOx at the parts per billion level: ~$0.90/ton CO_2 captured. Process and cooling water costs add another ~$3/ton CO_2 captured.

A little more than half of the operating cost (maintenance and labor) is proportional to the total capital cost: ~$90/ton of CO_2 captured and ~$120/ton of CO_2 captured for the lower and higher of the two capital cost estimates, respectively. The corresponding total operating costs are then ~$170/ton CO_2 captured and ~$200/ton CO_2 captured. The other operating costs (energy, chemicals and water) are independent of the capital cost.

Finally, the corresponding values of the total cost (the sum of capital and operating costs) are about $430 per ton of CO_2 captured and about $550 per ton of CO_2 captured, as shown in Table 2.5.

Table 2.5. Cost estimates for a DAC system using the sodium/calcium hydroxide and cost comparison with the coal-power PCC system from Table 2.2. (Costs in $/ton CO$_2$ are italicized.)

	Post-Combustion Capture: Coal Power	Air-Capture: Hydroxide Absorbent (Optimistic)	Air-Capture: Hydroxide Absorbent (Realistic)
CO$_2$ Captured (Tons per annum)	2,790,000	1,000,000	1,000,000
Capital Cost Estimate			
Purchased Equipment Cost ($ millions)	$113	$480	$480
Multiplier to Convert Equipment to Installed Cost	4.5	4.5	6.0
Total Installed Capital Cost ($ millions)	$500	$2,200	$2,900
Depreciation over 20 years ($/ton CO$_2$ captured)	*$9*	*$110*	*$150*
7% Return of Investment (ROI) ($/ton CO$_2$ captured)	*$13*	*$150*	*$200*
Depreciation + ROI ($/ton CO$_2$ captured)	*$22*	*$260*	*$350*
Operating Cost			
Maintenance ($ millions per annum)	$20	$70	$90
Labor ($ millions per annum)	$8	$20	$30
Consumables (Chemicals, Water) ($ millions per annum)	$12	$4	$4
Maintenance, Labor and Chemicals ($/ton CO$_2$ captured)	*$14*	*$90*	*$120*
Fuel Consumption (million BTU per annum)	102,000	7,600,000	7,600,000
Fuel Cost ($ per million BTU)	$6	$6	$6
Fuel Cost ($ millions per annum)	$1	$46	$46
Fuel Cost ($/ton CO$_2$ Captured)	*$0.22*	*$46*	*$46*
Power Consumption (MWhr per annum)	1,030,000	490,000	490,000
Power Cost ($ per MWhr)	$71	$71	$71
Power Cost ($ millions per annum)	$73	$35	$35
Power Cost ($/ton CO$_2$ captured)	*$26*	*$35*	*$35*
Total Annual Operating Cost ($ millions)	$114	$170	$200
Operating Cost ($/ton CO$_2$ captured)	*$40*	*$170*	*$200*
Cost per Ton CO$_2$ Captured			
Capital Cost ($/ton CO$_2$ captured)	*$22*	*$260*	*$350*
Operating Cost ($/ton CO$_2$ captured)	*$40*	*$170*	*$200*
Total Cost ($/ton CO$_2$ captured)	***$62***	***$430***	***$550***
Cost per Ton CO$_2$ Change in Atmospheric CO$_2$ Content ("Avoided Cost")			
Avoided CO$_2$ as a fraction of CO$_2$ captured at the device	0.78	0.70	0.70
Capital Cost ($/ton CO$_2$ avoided)	*$30*	*$370*	*$500*
Operating Cost ($/ton CO$_2$ avoided)	*$50*	*$240*	*$280*
Total Cost ($/ton CO$_2$ avoided)	***$80***	***$610***	***$780***

Energy cost vs. the thermodynamic minimum

The energy penalty per ton of CO_2 captured of 1.78 GJ_e of electricity plus 8.1 GJ_t of heat can be used to calculate a total primary energy requirement, after an assumption about the efficiency of the conversion of primary energy to electricity is made. If the efficiency is 100% the total primary energy requirement is 9.9 GJ per ton CO_2 captured, whereas it is 12.5 GJ/tCO_2 if the conversion efficiency is only 40%. These figures can be compared with the thermodynamic minimum for capturing 50% of the CO_2 from air at 298K that initially contains 500 ppm of CO_2, and compressing it. These minimum values are 445 MJ/tCO_2 for capture[19] and 218 MJ/ton work for CO_2 compression; thus the thermodynamic minimum to energy penalty is ~660 MJ/tCO_2.

It results that assuming perfect conversion efficiency leads to a penalty that is 15 times the thermodynamic minimum, whereas the penalty increases to 19 times the thermodynamic minimum when the efficiency is 40%. Since the corresponding ratios for the PCC case are 3.5 and 9, the DAC system is estimated to be more energy intensive relative to its thermodynamic minimum than the PCC system.

Net carbon and "avoided cost"

Both thermal energy and electricity are required for the DAC process modeled here. When either of these is provided by an energy source with associated CO_2 emissions, the net CO_2 removal from the atmosphere is reduced. In this analysis, natural gas provides the thermal energy for the kiln that regenerates CaO and releases CO_2. By contrast, electricity is assumed to be produced remotely by a grid with the average carbon-intensity of today's U.S. grid (610 kg CO_2/Mwh). The associated CO_2 production per ton of CO_2 captured from the air is roughly 0.4 tons CO_2 from the natural gas thermal energy source and 0.3 tons CO_2 from the electricity.

Either or both of these CO_2 sources could be produced locally with associated CO_2 capture. In the analysis here, it is assumed that the CO_2 emissions produced from burning natural gas in the calciner do not contribute to CO_2 emissions, because they are captured from the kiln effluent. The cost consequences of capturing and compressing this additional CO_2 from the natural gas are taken into account in the analysis. But the electricity emissions are not captured, since they are from the grid. The average carbon-intensity of today's U.S. electric grid is assumed to be 610 kg CO_2/MWh, the same grid carbon intensity as was assumed for the PCC plant in the previous section. Since the capture plant requires 0.49 MWh of power to capture 1 ton of CO_2 from the air, about 300 kg of CO_2 will be emitted at the remote power plants for each ton of CO_2 captured at the DAC plant.

As a result, the lower values of the annualized capital and operating costs for the DAC system become $370 and $240 per ton of CO_2 avoided, respectively, and the total cost becomes ~$610 per ton CO_2 avoided. The higher total cost becomes ~$780 per ton CO_2 avoided. As with the PCC example in the previous section, it is important to note that neither estimate is a true avoided cost, as it does not include the cost of CO_2 transport and sequestration, which, if included, would further increase the total cost of avoided carbon dioxide.[20]

An alternate strategy would be to produce the power onsite from natural gas and to capture the emitted CO_2, as is done for the natural gas that provides the thermal energy. The additional CO_2 associated with on-site electricity would further increase the size and power demand of the compressor and the CO_2 storage volume. This strategy is not considered here.

Accuracy of the cost estimate

The lack of experimental results for individual steps, such as CO_2 absorption from air and the oxygen-fired kiln, and for the integrated process suggests that the preliminary cost estimate for the DAC system can only be approximate. The DAC cost estimates above are what industry analysts call high-level estimates, often characterized as having an accuracy no better than +/- 50%. Industrial experience has shown that when plants are actually built, the +50% is a far more likely occurrence than the -50%.

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19   500 ppm CO_2 in incoming air is assumed here. The corresponding value for 400 ppm air, 458 kJ/kg, is calculated in Box 2.2. See Table 2.B2.1.

20   Assuming that fan power is proportional to pressure drop, and assuming a considerably larger pressure drop through the contactor—2000 Pa rather than the 300Pa value used above—but retaining all other assumptions and inputs, nine CO_2 molecules are emitted at power plants for each ten CO_2 molecules removed from the atmosphere at the DAC, and the system is hopeless. Indeed, only stringent combinations of small pressure drop through the contactor and low-carbon power are consistent with a viable DAC system, from the perspective of net carbon.

As with most chemical conversion processes, there are likely to be design trade-offs between capital and operating costs. Innovative designs may appear to be able to reduce both capital and operating costs, but advancements need to be reduced to practice in working systems.

For example, it has been proposed to exploit some of the special process specifications of the DAC system [33]. Commercial absorbers generally use countercurrent contact between gas and liquid and are designed for high absorption (capture) rates of 90% or more. The goal is to capture very efficiently as much as possible of a toxic pollutant or of a precious by-product. By contrast the design of the air contactor in a DAC system, also driven by capital and operating costs, is likely to target a lower capture rate (as low as 50%, as in the reference design above), because the efficiency of contact and mass transfer between gas and liquid is likely to be less important than minimization of pressure drop. Therefore, one can envision the use of cross-flow air-liquid contact configurations, as seen in cooling towers or water treatment plants, where the packing material facilitating the gas-liquid contact has a more open structure (and lower cost) than the commercial high-performance packing considered in the literature and above [34]. This approach might lead to liquid-to-gas molar ratios as much as ten times smaller than the present DAC example (see Table 2.3), which might even be obtained by intermittent liquid flow, as suggested recently [33]. Such designs may permit lower capital and operating costs to be realized, but the operability of such low liquid-to-gas-ratio systems through continuous, cyclic operation remains to be demonstrated.

Improving the front end of the DAC system could lower its capital costs, but unless the sorbent is changed from NaOH or a different sorbent recovery process is used with NaOH than the two-cycle sodium-calcium system explored above, the high energy penalty of the back end would remain. (See and compare Tables 2.3 and 2.4). In Chapter 3 of this report, a framework for discussing design innovation is presented that places process innovations in a context that encourages consideration of the entire DAC system.

2.4 Cost comparisons

Comparing the PCC and DAC cost estimates (see Table 2.5), the two DAC avoided costs, at $610/tCO_2$, and $780/tCO_2$, are approximately eight and ten times higher, respectively, than the cost of post-combustion capture. These costs are also approximately an order of magnitude higher than estimates of the costs of many climate-change mitigation strategies under active development, including energy efficiency in many contexts, CO_2 capture from large industrial processes, the less expensive forms of renewable energy, and, perhaps, nuclear-fission power [50]. The two cost estimates for DAC here are considerably higher than two cost estimates for systems deployable today: $140/tCO_2$ in Keith et al., 2005 [36] and $200/tCO_2$ in Lackner, 2009 [51]. See also Pielke, 2009 [52].

None of the costs in this chapter include the costs of dealing with CO_2 beyond the boundary of the facility, which is expected to be smaller than the capture cost for either PCC or DAC. This cost could in some cases be less for DAC systems, if they were sited close to favorable storage sites.

In general, the local operating conditions and constraints for DAC and PCC are markedly different. For PCC the input flue gas and the entire capture system are isolated from the local environment in a regulated and closed system. But, as discussed in Section 1.4, for DAC local weather variables and air pollution may restrict DAC siting options and/or constrain absorber performance.

Chapter 3 discusses the potential for improving the performance of both PCC and DAC systems through basic research. One message is that, in general, progress in DAC systems is likely to produce progress in PCC systems as well, although there might be specific technical solutions or material choices that bring value to the DAC system and not to the PCC process because of the broadly different operating conditions and process specifications.

Key Messages

- *Even if crudely, at least one DAC system allows technical and economic analysis.* The DAC system chosen as a case study absorbs CO_2 in a sodium hydroxide solution and regenerates the sodium hydroxide using technology similar to that used in the paper industry. However, even this system contains unproven components such as the oxygen-fired kiln.

- *The estimated capture cost of this DAC system is seven to nine times higher than the estimated cost of a reference post-combustion-capture system, and the estimated avoided cost is eight to ten times higher.* Using a common methodology and many common cost assumptions, costs are estimated for both this particular DAC system and a particular PCC system retrofitted to a coal power plant. The respective cost estimates are $430 to $550 and $60 per ton of CO_2 captured, using parameters for the DAC process at the optimistic end of the realistic range. The cost of CO_2 *captured* is also the cost of CO_2 *avoided*, if there are no CO_2 emissions from the associated energy sources, assuming all other costs are unchanged. The costs here are $610 to $780 and $80 per ton of CO_2 avoided, respectively, for a grid with the carbon-intensity of the present US power grid (~610 $kgCO_2/MWh$). These DAC and PCC cost estimates are for facilities that have the potential to be built today. They do not allow for cost reductions for subsequent facilities resulting from learning by doing, nor do they bear on the extent to which costs can be reduced by completely different designs.

- *The electricity supply for a DAC facility strongly affects "net-carbon."* In the reference DAC design, the estimated power expenditure of 0.49 MWh/tCO_2 captured results in the emission of approximately 300 kg of CO_2 at power plants for each ton of CO_2 removed the air, if the power comes from an average power plant on today's US grid. A decarbonized grid would allow the convergence of the cost of CO_2 captured and the cost of CO_2 avoided. An alternate strategy would be to produce the power onsite and to capture the emitted CO_2 from the power source, as is done for the natural gas that provides the thermal energy in the reference DAC design. The additional CO_2 associated with on-site electricity would further increase the size and power demand of the compressor and the CO_2 storage volume.

- *The largest uncertainty in the DAC cost is the cost of the air contactor.* It would be much less costly if an operable process could be designed with a more open system, such as is used in cooling towers. The practicality of such a system depends on the ability to provide good contact between the air and the sorbent, while minimizing physical losses of the absorbent solution through mechanisms such as misting or chemical reactions with particulates and acid gases in the air.

Appendix 2A. Methods for Assessing Costs

One objective of this chapter has been to produce an initial estimate of both the capital and operating costs of a complete, commercial-scale direct air capture facility that could plausibly be built today to capture one million tons of CO_2 per year, and then, using the same methodology, to generate an estimate for post-combustion capture (PCC) of CO_2 in order to provide a comparative benchmark for the direct air capture estimate. The purchased equipment and operating cost used to generate the PCC estimate is taken from an advanced comprehensive study for CO_2 capture from coal plants [9]. A second objective has been to explain the procedures of industrial cost analysis.

Tables 2.2 and 2.5 summarize the cost estimates that were developed for this report with the preliminary project screening techniques used in industry. These traditional economic evaluation techniques produce rough, high-level cost estimates. The capital cost is estimated by applying a "rule of thumb" multiplying factor to the estimated purchase cost of only the major Inside Battery Limits (ISBL) equipment purchases. Such a multiplicative factor is routinely used in industry for preliminary cost estimates. It takes into account the costs of engineering, site preparation, foundations, structures, equipment, installation, utilities piping, electrical and control systems, commissioning, start-up, and contingency for underestimated or "missed" components.

The product of the multiplying factor times the ISBL purchased equipment cost is the "fully built up" capital cost. The multiplicative factor can be understood as a reflection of decades of actual project execution experience. That experience indicates that costs are often underestimated for preparing the site, moving major pieces of equipment to the site, and installing and connecting the major equipment at the site. Costs of instrumentation, piping, control, monitoring and safety related devices needed at the site are also frequently omitted or underestimated. Underestimates or omissions of "off-site" costs, such as roads, office buildings, electric sub-stations, sewer systems and water treatment plants are also common.

What multiplicative factor should be used? The chemical process and refining industries uses a factor which itself is the product of factors. The first is the ISBL factor itself, which takes into account only additional costs directly related to the IBSL equipment such as piping and instrumentation. For continuous processes involving gases and liquids, typical of most chemical and oil refining processes, industry uses a "rule of thumb" factor of 4. A process in which the equipment is complex and expensive and thus represents a larger portion of the cost, such as a process involving significant solids handling, packaging, or exotic materials of construction, has an ISBL factor of 3-3.5. For processes that are dominated by very expensive and very complex mechanical equipment, such as a gas turbine, the ISBL factor can be as low as 2. The choice of an ISBL factor of 2.7 for both post-combustion capture with MEA and air capture with NaOH reflects the relative complexity, number, and size of the major pieces of equipment involved in both cases.

A second factor takes into account that stand-alone plants have additional process-related items that are outside battery limits (OSBL), including tank farms for raw materials and products, warehousing, utility systems (steam boilers, cooling towers, wastewater treatment, electricity generation, etc.), electrical substations, railroad tracks, and the like. Administration, control, maintenance buildings, cafeterias, roads, parking lots, security, and other general plant items are also included in the OSBL estimate. In stand-alone facilities that need to generate their own utilities, such as might be the case for a CO_2 air capture facility in a remote location, some of these OSBL capital costs can be substantial and must be estimated separately using the same techniques used for ISBL capital costs. On the other hand, if the utility services can be purchased, the charges are operating costs rather than capital costs. In this analysis, utilities are purchased, and as a result, the utility charges are included in the operating costs. A useful "rule of thumb" is that OSBL capital costs are about 1/3 of ISBL capital costs. As a result, to account for OSBL capital costs the ISBL factor is raised from 2.7 to 3.6.

A final adjustment of the multiplicative factor is a contingency factor that takes into account that at the preliminary project screening stage there is large uncertainty in two principal areas:

1. The process may not work as conceived

2. There may be errors in the chemical, physical, and/or business data on which the design estimate is based.

For early commercial deployments, especially first-of-a-kind plants, these uncertainties appear frequently and may add an additional 20-50% to the overall capital cost. For this study, a low contingency factor of 25% has been added. This brings the overall capital cost multiplier from purchased major equipment through total plant cost to 4.5. This value is relatively low. A more appropriate capital cost factor, treating a first-of-a-kind air capture facility like any new plant commercializing a new chemical process, would be at least 6.

The following additional economic assumptions are made:

- The ISBL purchased equipment costs are estimated on a common 2009 basis to remove effects of inflation.

- The capital depreciation contribution per ton of CO_2 captured assumes a 20-year plant life, and thus is 5% of the full capital cost.   No terminal value of the plant is assumed, as waste disposal and site remediation is likely to offset residual value of equipment and facilities.

- The return-on-capital component assumes a 7% average return on the full capital cost invested, a percentage meant to reflect a "utility return." No tax effects are included.

- The facility is assumed to operate with long-run average on-line factor of 90% (i.e., its annual quantity of CO_2 captured equals what it would capture operating at full capacity, 7884 hours per year).

- Respectively, for the PCC and DAC plants, the annual maintenance cost is assumed to be 4% and 3% of total capital cost, and the labor cost is assumed to be 40% and 30% of the maintenance cost. In the PCC example, operations are more complex and tightly integrated, hence the higher factors relative to the DAC example.

The reference price for the foregone power at the PCC plant is $71/MWh—a rough estimate of the cost of power production from a new-build coal fired power plant, including a modest 7% return on capital.

- The annualized total cost of CO_2 capture is the sum of depreciation, return on investment, and all fixed and variable operating costs.

- Components of annualized total cost are divided by tons of CO_2 captured during the year to arrive at components of *the cost per ton of* CO_2 *captured.*

- *The cost per ton of* CO_2 *avoided* is calculated by making allowance for greenhouse gas emissions associated with power and heat used during the process. For PCC, heat (steam) and power requirements result in loss of capacity which is compensated for by grid power. For DAC, the CO_2 produced from natural gas to provide high-temperature heat is assumed to produce no emissions via its capture and co-storage with the CO_2 captured from the air. Electricity for DAC is assumed to be provided from the grid. In both cases, a carbon intensity of 610 kg CO_2 per MWh is the reference carbon intensity, approximately the carbon intensity of average power in the U.S. today.

If someday sufficient experimental data were available for more reliable cost estimates, additional analysis steps could be taken:

- Design of a process flowsheet. The flowsheet would include CO_2 product preparation and pipeline specifications for transport to the sequestration site at a minimum pressure of 100 atmospheres.

- Development of both heat and material balances for the process flowsheet that are consistent with the experimental data.

- Preliminary equipment designs and specifications for every major unit operation.

- Process capital cost estimates (purchased equipment cost) based on preliminary equipment design.

- Process capital cost estimates for the processes within the core plant, called inside battery limits (ISBL) costs. These costs include purchased equipment costs, installation costs, contingency, and other plant costs (location, foundations, structural, piping, utilities, engineering, etc).

- Operating cost estimate based on energy inputs, consumables (such as absorbent replacement), labor, maintenance, etc.

- Capital cost estimates for additional outside battery limits (OSBL) capital expenditures (tanks, warehouses, heat and power utilities, waste treatment, etc.), working capital, general plant costs (administrative buildings, roads and railroads, etc), and other burdens on operating costs (administrative, research/process improvement, marketing, etc).

Agreed financial methods and parameters for performing economic analyses encompass net present value costing, legal depreciation schedules, tax rates and incentives, cost of capital, internal rates of return, project life, operating rate, etc.

Chapter 3: The Research Frontier for Direct Air Capture

3.1 The CO_2 Capture Cycle

3.2 Binding of CO_2

3.3 Release of CO_2

3.4 Integration

3.5 Features of the research frontier for Direct Air Capture of CO_2

In Chapter 3 the potential for direct air capture (DAC) of CO_2 from the atmosphere is assessed. Chapter 2 illustrated an example of DAC based in large part on established industrial processes and estimated that the process would cost an order of magnitude more than post-combustion capture (PCC) today. Both PCC and DAC were shown to be capital intensive and to have significant operating costs. This chapter moves beyond comparisons of DAC and PCC to investigate the potential design space for advancing DAC. As DAC faces novel challenges relative to more conventional CO_2 capture systems, the optimal design parameters for a DAC system could be notably different from existing and evolving technologies for PCC. The approach includes systematic examination of the basic chemistry and materials science underlying each individual step in the air-capture process. As both DAC and PCC share similar process steps, particular challenges and opportunities associated with DAC are described, with the recognition that there is considerable overlap with PCC processes.

Over 50 years of research has been carried out for the separation of acid gases, including CO_2, from process streams and effluents. For air capture, there has been limited effort to date, with some unique approaches, e.g., involving solid materials in place of fluids, which may have the potential for advancements. Transformational changes will likely require the integration of achievements in several fields of materials science, as well as chemical and process engineering.

In this chapter, an idealization of CO_2 capture (whether from industrial effluent or air) as a seven-step process is presented and areas of opportunity identified for each step. The risk from this step-wise view is that progress along a single parameter may or may not be helpful for the overall process. Improvements in one process step may create additional challenges in other process steps and/or simply lead to trade-offs between capital and operating cost without reducing the cost of the overall process. A good example is the trade-off where stronger, more efficient binding of CO_2 in the capture reaction results in greater energy requirements for regeneration. Therefore a DAC process needs to be assessed on an integrated basis with respect to both its potential operational effectiveness and the overall economics of CO_2 capture. Over time, advancements in most, if not all, of the process steps may be required for a novel air capture system to be successfully demonstrated, and/or to reduce the costs of DAC significantly in real terms, and possibly begin to close the gap with PCC.

At the close of the discussion of each step, there is a list of questions/challenges that represent potential research opportunities. In aggregate, they indicate the possible scope of a potential research agenda for the field.

3.1 The CO_2 Capture Cycle

For both PCC and DAC, the CO_2 capture process involves the binding and release of CO_2 in a cyclic process, where the material that binds the CO_2 is the vehicle for the cyclic operation.   To better understand the underlying science, it helps to subdivide the CO_2 sorption-desorption cycle into seven steps, four that involve binding the CO_2 and three that involve the release of the CO_2 and restore the binding material to a capture-ready state.

The four binding steps are:

1. Transport of a gas mixture containing CO_2 to the boundary of the medium containing the binding material

2. Transfer of the CO_2 across an interface, from the gas phase into the medium that contains the binding material

3. Transport of the CO_2 within the medium that contains the binding material, to the binding site

4. Reaction of CO_2 at the binding site

The three steps required to complete the cycle and prepare sequestration-ready CO_2 are:

5. Release of CO_2 from the binding site

6. Regeneration of the binding material and/or medium

7. Purification and compression of the CO_2

A simplification is being made in the sequence above as step 5 is really a composite representing the reversal of the first four steps involving CO_2 binding. This simplification is being made to avoid repetition of some of the points involved with steps 1 through 3 and allow focus on the key CO_2 release step, the reversal of step 4. In addition, step 7 isn't a part of the capture cycle, but would be required if the captured CO_2 is to be readied for underground sequestration.

The efficient, cost-effective integration of these seven steps may potentially improve the cost effectiveness of CO_2 capture. For any given process configuration, the cycle time would ideally be as short as possible in order to maximize the utilization of installed equipment. In addition, operating costs could be reduced if components, such as binding materials, are long lived, retaining their effectiveness through a very large number of cycles. In Box 3.1, the cost of the sorbent material per ton of CO_2 captured is assessed by considering the life of the absorber and the sorption-desorption cycle as a "swing" with an amplitude and period.

Note that the processes for CO_2 capture from flue gas and air that are described in Chapter 2 are *ab*sorption processes, i.e., CO_2 reacts with a base in a bulk aqueous solution. In addition to absorption, *ad*sorption technologies, in which CO_2 binds to the surface of a solid material, may also be plausible for air capture systems. Both absorption and adsorption involve specific CO_2 binding sites, and the steps of the binding process apply to both absorption and adsorption.

Section 3.2 describes the four CO_2 binding steps, and Section 3.3 describes the three CO_2 release steps. Together, they illustrate the challenges and opportunities for the optimization of the full carbon capture cycle. It should be noted that while these have been identified based on the discussions hitherto on direct air capture, advances for direct air capture processes may also have a bearing on post-combustion capture systems. Given the energy requirements for CO_2 capture in general, and as shown in Chapter 2 for direct air capture in particular, significant advances in PCC and its deployment may be a prerequisite in many locations to produce low-carbon heat and power for DAC should direct air capture become required.

Box 3.1. Cost Implications of Swing Duration and Depth and Sorbent Lifetime

Both liquid absorbents and solid adsorbents contribute a cost to a capture process that reflects their durability. A contaminated liquid is usually "cleaned" by gradually and steadily removing contaminants and blending in a fresh solution, while a solid that has degraded is typically completely replaced. Here, the consequences of a solid adsorbent of finite lifetime are worked out.

A sorbent is assumed to go through a cycle (a "swing") of either pressure or temperature or both. Hence, "pressure-swing sorption" or "temperature-swing sorption"), characterized by a sorption interval followed by a desorption interval. Four variables describe this process.

1. The time required for an entire swing, the *Swingtime* (seconds).

2. The number of moles of CO$_2$ sorbed and desorbed per swing, normalized by some measure of the quantity of sorbent, the *ReversibleCapacity*. The reversible capacity can be normalized by the mass, volume, or surface area of the sorbent (moles of CO$_2$ per kg, m^3 or m^2 of sorbent). The average rate at which CO$_2$ is sorbed and desorbed is the fraction, *ReversibleCapacity/ Swingtime*, with the units of moles of CO$_2$ per unit time per unit of sorbent.

3. The *Cost* of the sorbent, normalized in the same units as *ReversibleCapacity*. A sorbent that needs to be replaced several times during the lifetime of the capture facility is best treated as an operating cost averaged over replacement periods.

4. The *Lifetime* (seconds) is the time between sorbent replacements. Over the lifetime of the sorbent, it will undergo a number of swings that is the ratio *Lifetime/Swingtime,* and it will capture a quantity of CO$_2$ given by *ReversibleCapacity*Lifetime/Swingtime.*

The cost per ton of CO$_2$ captured arising from sorbent consumptive use is the quantity of interest. This cost is obtained by dividing the unit cost of the sorbent by the quantity of CO$_2$ captured over its lifetime. Algebraically, this cost is

$$\frac{CostSorbentConsumption}{tonCO_2} = \frac{Cost}{ReversibleCapacity \cdot \dfrac{Lifetime}{Swingtime}} = \frac{Cost \cdot Swingtime}{ReversibleCapacity \cdot Lifetime}$$

A wide range of values can be chosen for each parameter. For specificity, consider a *Swingtime* of 2 hours and a *Lifetime* of 1 year, so the sorbent performs 4,380 swings before replacement. Averaged over the swings throughout the sorbent lifetime, assume a *ReversibleCapacity* of 1.0 moles of CO$_2$/kg sorbent per swing, so that 4,380 moles of CO$_2$, or approximately 0.20 tons of CO$_2$, are sorbed per kg of sorbent over its lifetime. Also choose a *Cost* for the fabricated sorbent of $10/kg. The sorbent cost contribution to the overall cost, with these inputs, is $50/tCO$_2$ captured.

3.2 Binding of CO$_2$

The first three steps of the capture cycle involve moving CO$_2$ from the gas to the binding site, where, in Step 4, the binding occurs. Figure 3.1 is a schematic of the four steps. In step 1, the CO$_2$ is transferred through the gas phase to the interface with a liquid or a solid containing the binding sites. In step 2, the CO$_2$ is transferred across the interface into the liquid or onto the surface of the solid. In step 3, the CO$_2$ moves to the reaction site, labeled B. In step 4, the CO$_2$ reacts with the binding material to form a complex, labeled BCO$_2$. Any one of these four steps could be the rate-limiting step of the binding process, and thereby act as a bottleneck.

Figure 3.1. Diagram of the four steps involved in binding
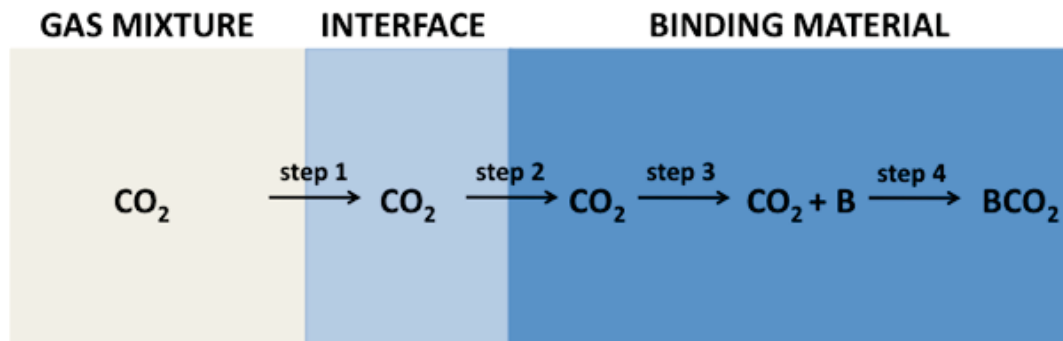
These consecutive steps are linked, where changes in a step later in the chain may impact earlier steps. For example, as CO_2 reacts with a binding site B to form the BCO_2 complex, additional CO_2 may move into the phase containing the binding sites, followed by more CO_2 transitioning through the interface from the gas phase.

Step 1: Transport of gas containing CO_2 to the binding medium

In PCC for a coal fired power plant, the starting point is the effluent available as a confined stream that has already gone through flue-gas desulphurization. Compressors and pumps are used to establish countercurrent flow between the gas stream and the MEA solution in an absorption column. Energy is required to move the gas and liquid, and the contactor is designed to minimize power use without compromising the amount of CO_2 captured.

The starting point for DAC is unconfined ambient air. As a result much larger volumes of gas (>250 times at similar capture percentages) are involved per quantity of CO_2 in DAC relative to PCC, and there are two conflicting demands on the design of the contactor used for CO_2 capture from air. On the one hand, the largest possible interface with the air for a given contactor volume may be desired, given the low CO_2 concentration in air. This objective may be accomplished by sending the air through a contactor with many narrow passages. On the other hand, the energy cost required to move the air through the high-surface-area contactor must not be high. The energy to move air is proportional to the pressure drop that needs to be overcome, and the pressure drop, in turn, for relevant cases, is inversely proportional to the transverse area of the passage. This effect on contactor design is discussed the Appendix 3A.

The DAC system discussed in Chapter 2 and Appendix 3A assumes that electric fans are used to drive air through the contactor structure. Some entirely different air capture schemes have been proposed that remove or reduce this energy cost by relying on ambient wind to move all, or some, of the CO_2 to a sorbent [10]. As noted in Chapter 1, a system driven by wind must operate not only intermittently but with a very low pressure drop through the contactor (see footnote 9).

Among the step 1 questions/challenges are:

- Can geographic locations and technologies be identified where the use of ambient wind substantially reduces the energy cost associated with moving air to the medium containing the CO_2 capture sites without compromising the efficiency of the absorbent/adsorbent?

- Can the impacts of particulate matter, gaseous contaminants, wind speed and rain on the absorbent/adsorbent be limited or eliminated?

- Can low-temperature waste process heat that is not lost to the environment assist in powering the fans that move air through the absorbent/adsorbent?

Step 2: Transfer of CO_2 across the interface into the medium containing the binding sites

Regardless of the transition rate for CO_2 across the interface into the medium containing the binding sites, an increase in the interfacial area will increase effectiveness, as a greater opportunity for CO_2 transfer is then available. In PCC the CO_2 in flue gas reacts with a base in an aqueous solution, and the absorption column internals are used to create a large interface between the solution and the flue gas [53].

In packed absorption columns, the absorbent solution flows over and coats a high-surface-area volume of packing material. The effective surface area of the interface is typically in the range of 125-500 square meters per cubic meter (m^2/m^3) of packed-column volume. The packing is designed to achieve good contact between the gas and the liquid and to minimize the pressure drop across the column. Packed columns use randomly stacked or structured packings made of stainless steel, ceramic or plastic depending on the absorption process conditions and chemicals. The choice of the type of packing is based on a trade-off between pressure drop and mass transfer efficiency

In addition to packed columns, there are a variety of other contacting devices to bring the absorbent liquid into contact with the CO_2-containing gaseous effluent, such as spray towers (as used in sulfur dioxide scrubbers), liquid membrane [54], plate columns, and variants that are optimized for wind enhancements.

For DAC, in contrast to PCC, the supply of feed gas (air) is effectively limitless. As a consequence, the goals for DAC and PCC with respect to CO_2 removal may not be the same. The goal for PCC is to remove as much of the CO_2 from the effluent as is practical: however, as a result of the limitless supply of feed, the goal of DAC is to remove CO_2 efficiently, but not necessarily a high fraction of the CO_2. Accordingly, a distinction in the conceptual approach can be made for the two processes. For PCC the objective is for all of the flue gas to contact the absorbing liquid; otherwise, the flue gas that does not contact the liquid will leave the stack with a higher CO_2 concentration than desired. For DAC (with a liquid absorbent) the objective is for all of the absorbent liquid to contact enough air to use the absorbent's capacity effectively; otherwise, the binding agent is not being used to its maximum potential in an already low CO_2-loading environment due to the dilute nature of CO_2 in air. As a result, practical designs for an absorber for DAC may be quite different from the designs used for PCC.

One possibility for DAC may be to use a design similar to that used in cross-flow cooling towers, for the absorber. In a cooling tower, warm cooling water rejects its heat through evaporation into the passing air, and effective cooling requires that all of the water contacts air—not that all of the passing air contacts water. To assure that nearly all of the water contacts some air, the air flows through channels in a structured material whose internals have 50-150 m^2/m^3 of contact surface area. In the Chapter 2 DAC example, fan-blown air is moved in cross-flow with absorbing solution. Such lower-performance packing materials are less costly than those used in PCC, and, as well, their more open design reduces the pressure drop. However in order to effectively use a cross-flow cooling tower type design for DAC, it will be necessary to avoid or mitigate excessive evaporative loss of solvent liquid and/or entrainment of the absorbent solution ("drift" or "misting") resulting from the high air-flow rates anticipated in DAC systems. Minimizing or eliminating such losses will be important not so much because of cost but because the chemicals in the absorbent solution, such as containing strong bases, are likely to be hazardous. In addition, excessive solvent evaporation may result in fouling of the surfaces in the absorber from precipitation of solids from solution.

Rather than using *ab*sorption for the air capture of CO_2, another approach uses systems based on *ad*sorption in which CO_2 binds to the surface of a solid material. A potential key advantage of a solid adsorbent is the avoidance of solution losses that would occur when a liquid absorbent interacts with air in a system open to the environment.

Binding of CO_2 to an adsorbent occurs at basic sites in, or attached to, the surface of a fixed solid structure, or to counter-anions (e.g., OH^-) associated with a positively charged functional group (e.g. alkyl ammonium) that is incorporated into the backbone of a solid material such as a polymer resin (as in ion exchange resins used in water treatment) or metal oxide [55]. As with absorption by flowing liquids, efficient adsorption onto fixed solids requires a high-surface-area interface and the effective use of a high fraction of the binding sites. High surface area is achieved by using solid support materials which contain small pores, often referred to as micropores, whose diameters range from nanometers to micrometers. The basic sites that bind CO_2 are then added to the surface of the pores.

Such microporous solid structures result in effective surface areas of 10s to 100s of square meters per gram of material. This property translates into tens to hundreds of *millions* of square meters of surface area per cubic meter, many thousands of times larger than the corresponding values for the absorption column and cooling tower packing materials reported above. However, because of the surface tension of water and the presence of an average of ~0.5% water in ambient air, water vapor condenses into the micropores of these high surface area materials. These materials, as currently available, may contain as much as 50% water by weight at ambient conditions. As a result, adsorption chemistry within the solid pores often parallels aqueous solution chemistry. For DAC applications using such materials, transport of CO_2 to binding sites after crossing the interface (Step 3) may involve diffusion through a liquid. Additionally, although water is a weaker acid than CO_2, the presence of an excess of water near the binding sites may interfere with CO_2 binding at the basic sites.

Among the step 2 questions/challenges are:

- Can low-cost packing structures for absorption processes be designed that create a large surface area for contact between the air and liquids in DAC applications, while minimizing pressure drop and losses of liquid by evaporation and misting?

- Can high surface area solids be functionalized with CO_2 binding sites that don't contain significant amounts of condensed water at ambient conditions for use in DAC?

- Can effective physical structures be designed and constructed for contacting air with high surface area solid CO_2 adsorbents?

- Can liquid-phase CO_2 sorbents be developed that avoid volatility losses during the air capture process, maintain efficient mass-transfer properties, and are not hazardous?

Step 3: Transport of the CO_2 to the binding site

In Chapter Two, the PCC example utilized an aqueous solution of monoethanolamine (MEA) as the absorbing solution, and the DAC example used an absorption process with an aqueous solution of sodium hydroxide (NaOH, or lye). In these processes, the water matters. One needs to consider not just the diffusion to the binding sites but also the behavior of CO_2 in water prior to and during its reactions at the binding site. Also, as noted in the previous section, even on high-surface-area solids functionalized with binding sites, one needs to consider the impact of interactions of CO_2 with water in the pores.

Before considering what happens when CO_2 reaches the binding site, it is productive to consider what happens when CO_2 is dissolved in water, since the binding agent is typically in an aqueous solution. Four aqueous forms of the CO_2 need to be considered: carbon dioxide simply dissolved in solution, carbonic acid (H_2CO_3) which forms from the reaction of CO_2 with water, bicarbonate ion (HCO_3^-) which forms when carbonic acid loses a proton, and carbonate ion (CO_3^{2-}), which forms when the bicarbonate ion loses a proton. The four-component system can be approximated by considering each of these steps in sequence.

As the initial step for DAC, CO_2 in the air comes into equilibrium with CO_2 dissolved in water. Henry's Law states that the molar concentration of CO_2 in solution will be proportional to the partial pressure of CO_2 in the gas phase at the water-gas interface. One form of the Henry's Law constant for CO_2 and water at 25°C is 0.0339 moles per liter per atmosphere. Therefore, assuming a CO_2 concentration of 380 ppm in air at atmospheric pressure, its partial pressure is 380×10^{-6} atm and the equilibrium concentration of CO_2 in solution will be $\sim 1.3 \times 10^{-5}$ moles per liter.

In a second step, the water-solvated CO_2 will react with water to form H_2CO_3, carbonic acid. This step is slow, and may be the rate-limiting step in the CO_2 binding process in DAC. In nature, an enzyme, carbonic anhydrase, accelerates the formation of H_2CO_3 from CO_2 [56, 57]. The rate of the enzyme-catalyzed reaction is eight orders of magnitude faster than the reaction in neutral water without the enzyme. Carbonic anhydrase also assists the next step, the formation of bicarbonate ion, as the formation of the H_2CO_3 proceeds via formation of enzyme-bound HCO_3^-. See Box 3.2 for a detailed description.

Carbonic acid dissociates in water to form bicarbonate anion (HCO_3^-) via the reaction

$$H_2CO_3 \rightleftharpoons HCO_{3\ solvated}^- + H_{solvated}^+, \hspace{5cm} \text{(Reaction 3.1)}$$

The equilibrium constant, $K_{eq,}$ for the combination of the dissolution of CO_2 in water to form carbonic acid (H_2CO_3) and the ensuing disassociation reaction (Reaction 3.1) is only 4.5×10^{-7} moles per liter (25°C), therefore the reaction does not proceed very far to the right side of the equation. About 80% of the carbonic acid remains as solvated H_2CO_3. Because the system is electrically neutral, the positive and negative ions have the same concentration, which allows one to use the K_{eq} to calculate that the concentration of each is 2.5×10^{-6} moles per liter, which equates to a pH of 5.6 (pH is the negative logarithm of the hydrogen ion concentration in moles per liter) This value is only 25 times greater than the H^+ concentration in pure water (whose pH is 7.0), and as a result carbonic acid is considered a weak acid.

The bicarbonate anion, $HCO_{3\ solvated}^-$, can act as an acid, losing an H^+ becoming $CO_{3\ solvated}^{2-}$, or (see above) it can act as a base, gaining an H^+ to regenerate carbonic acid. The K_{eq} for the reaction

$$HCO_{3\ solvated}^- \rightleftharpoons CO_{3\ solvated}^{2-} + H_{solvated}^+ \hspace{5cm} \text{(Reaction 3.2)}$$

is $\sim 4.7 \times 10^{-11}$ moles per liter, which at a pH of 5.6 implies that the $CO_{3\ solvated}^{2-}$ concentration is less than $\sim 0.002\%$ of the $HCO_{3\ solvated}^-$ concentration.

Box 3.2. Carbonic Anhydrase—Accelerating the Reaction of CO$_2$ with H$_2$O

A common way to increase reaction rates without increasing the temperature is to add a catalyst, a chemical substance that increases the rate of a reaction without changing the thermodynamic properties, like reaction enthalpy, and without being consumed in the reaction. Carbonic anhydrase is a zinc-containing metalloenzyme that catalyzes the conversion of CO$_2$ to H$_2$CO$_3$ and HCO$_3$- in near neutral water at high rates, moderate binding energies and high selectivity [58]. A number of researchers are studying ways to use carbonic anhydrase, and similar biological or synthetic systems, to improve the efficiency of CO$_2$ capture.

The mechanism for the conversion from CO$_2$ to HCO$_3$- using carbonic anhydrase, and related catalysts, is shown in the figure below. The zinc atom binds to a water molecule and facilitates a conversion to OH-. The bound OH- ion binds to CO$_2$ in the same way that it would in an aqueous solution, and creates HCO$_3$-. The HCO$_3$- is released to the solution and is replaced by a H$_2$O to complete the catalytic cycle. The mechanism is simply run in reverse to regenerate the CO$_2$. Because carbonic anhydrase converts H$_2$O to OH- in the first step of this mechanism, there is a significant amount of H+ formed and released to solution. A buffer, such as a phosphate buffer commonly found in biological systems, is used to maintain the pH of the solution so that excess protons react with the phosphate and do not change the solution equilibrium. The rate constant of this reaction is 1x10^6 M^{-1}s^{-1}, 8 orders of magnitude higher than that of the CO$_2$ hydrolysis reaction in neutral water without the catalyst [59].
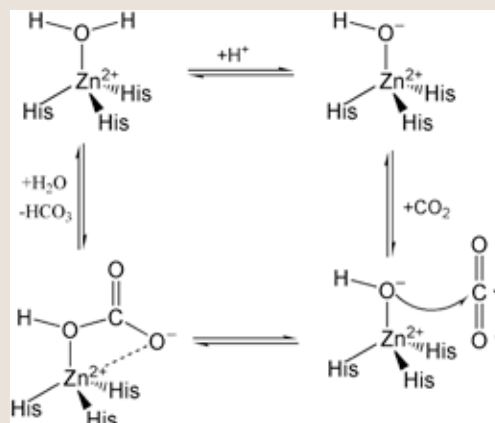
Figure 3.B2.1. The mechanism for the conversion of CO$_2$ to HCO$_3$- by carbonic anhydrase and related metalloenzymes.

Trachtenberg et al. [56] have proposed a carbonic anhydrase and membrane permeation based CO$_2$ capture process. There are three steps to this process; 1) CO$_2$ is converted to HCO$_3$- using carbonic anhydrase at the feed side gas-liquid interface, 2) HCO$_3$- diffuses through the liquid membrane, and 3) carbonic anhydrase converts HCO$_3$- back to CO$_2$ at the sweep side liquid-gas interface from which CO$_2$ exits the membrane. This description does not account for the interferent molecules in the gas mixture, such as N$_2$, O$_2$, SO$_x$ and NO$_x$ compounds. In addition, a method will have to be identified to recover the CO$_2$ from the sweep gas. As bicarbonate HCO$_3$- has higher solubility in the aqueous solution than N$_2$ and O$_2$ in the liquid membrane the concentration gradient promotes passage of CO$_2$ to the sweep side of the membrane. Ultimately, the explicit solubilities of the more interferent molecules such as SOx in the contained liquid membrane must be determined, and if they impact the performance of the carbonic anhydrase.

Clearly, there are a number of challenges to implementing this chemistry in a practical CO$_2$ capture system, either for post-combustion or air capture. The system is quite complex; a delicate balance of carbonic anhydrase and buffer concentration is needed to maintain ideal operating conditions. It is still unclear whether it will be scalable or economically viable. The catalytic activity of enzymes decreases when they are exposed to harsh conditions, like the elevated temperatures needed for regeneration. Thus, the expensive enzymes will need to be regularly replaced. It might be possible to synthesize catalysts in a lab setting that mimic the chemistry at the carbonic anhydrase active site but are more long-lived and less expensive. Similarly, it might be possible to use bioengineering or synthetic biology methods to identify an enzyme that performs the same function as carbonic anhydrase, but under conditions relevant for CO$_2$ capture. These catalysts do not need to have the same extraordinary catalytic activity of carbonic anhydrase; it is not necessary to achieve an 8 order of magnitude improvement to substantially improve performance. While there are a number of challenges to integrating catalysts into a CO$_2$ capture system, this type of system is one of the few, if not the only one, that successfully achieves the high absorption rate and moderate reaction enthalpies that are key for a successful CO$_2$ capture chemistry. Research is being done on carbonic-anhydrase-inspired catalysts for PCC, though the work is mostly confined to the bench-scale. Initial advances in these systems will primarily apply to PCC, but there may potentially be applications in DAC as well.

The formation of carbonic acid as the rate limiting step in the transformation of dissolved CO_2 into bicarbonate anion makes the potential concentration of carbonate species in aqueous solution a strong function of pH. Thus for seawater at pH 8.1 it is typical to have total carbonate species of around 2.3×10^{-3} moles per liter [60]. For strong bases the presence of one mole of base will convert one mole of carbonic acid to bicarbonate—however, these bases also interact chemically with the dissolved carbonate species as discussed in the next section.

Among the step 3 questions/challenges are:

- Could an inexpensive, robust, catalyst with a function similar to carbonic anhydrase, which accelerates the rate of carbonic acid formation in water, be added to absorbent solutions or base functionalized, high-surface-area solid supports used for DAC?

- For solid adsorbents, can a support material be developed that minimizes the adverse consequences of water in pores, thereby reducing the effective transit time of CO_2 to the binding sites?

Step 4: Reaction of CO_2 at the binding site

A necessary but not sufficient condition for a DAC process is an effective reaction of CO_2 binding at the site. In other words, once a CO_2 molecule binds, the back reaction that would release the CO_2 does not take place readily at the conditions under which the binding reaction occurs. The relative irreversibility of the binding step is especially critical if the bound CO_2 complex were to be isolated for later CO_2 release and sequestration. However, a greater irreversibility of initial binding creates a greater challenge for the step which leads to CO_2 release.

Reaction Chemistry

The chemical capture of CO_2 is accomplished in the PCC and DAC examples in Chapter 2 through the reaction of the acidic CO_2 molecule with a basic molecule. The central carbon atom in a CO_2 molecule possesses a partial positive charge as a result of the withdrawal of electron density from the carbon by the two electronegative oxygen atoms. CO_2 acts as an acid when its carbon atom receives electron density from any basic molecule, i.e., a molecule that can donate electron density. The bond is formed through the reaction:

$$CO_2 + B \rightleftharpoons BCO_2, \hspace{6cm} \text{(Reaction 3.3)}$$

where B is a generic base molecule. The stability of the BCO_2 complex must be optimized to ensure that the CO_2 molecule is firmly enough bound to be selectively removed from the input gas, but not so tightly bound that the energy requirements for regenerating the reactive base molecule and creating a concentrated CO_2 gas stream are excessive. This tradeoff highlights one of the primary tensions underlying the design of a DAC system: a strong bond between the base and CO_2 is desirable because of the low concentration of CO_2 in the atmosphere, but this leads to greater energy requirements to break this bond during the regeneration step.

There is a delicate balance between the binding strength, called reaction enthalpy in thermodynamics, and the energy associated with regeneration. The reaction enthalpy (ΔH) is negative for reactions where heat is produced and becomes more negative as the binding strength increases. However, the reaction enthalpy is only part of the thermodynamics story: there is also reaction entropy. When CO_2 binds to a base (B) in the Reaction 3.3, the two separate B and CO_2 molecules combine to form one CO_2-bound complex (BCO_2), which increases the order of the system. Thermodynamics refers to an increase in order of a system as a decrease in its entropy (ΔS). Entropy is a measure of disorder. The impact of the entropy change on a reaction is temperature-dependent. The key quantity that combines the effects of enthalpy and entropy change, known as the Gibbs Free Energy change (ΔG), is defined as the reaction enthalpy (ΔH) minus the product of reaction entropy (DS) and absolute temperature; i.e. $\Delta G = \Delta H - T\Delta S$ (for fixed T and pressure, P). A reaction will occur spontaneously when ΔG is negative. Thus, a reaction that releases heat (negative H) but increases the order of the system (negative $T\Delta S$) can either be spontaneous or not, depending on which term in the expression for ΔG is more negative. Specifically, the reaction of CO_2 with a solvent or sorbent will occur spontaneously if the heat released more than offsets the increase in order. Since, other things being equal, a higher temperature increases the magnitude of the second term ($T\Delta S$) in the expression for ΔG, there are many situations where a forward reaction may proceed spontaneously at a low temperature, but the reverse reaction may proceed spontaneously at a higher temperature.

The DAC and PCC examples from Chapter 2 utilize two different bases, OH- and MEA, respectively, to bind to CO_2. Descriptions and comparisons of the chemistries involved are found in Box 3.3.

Box 3.3 Two Capture Chemistries: Carbonate (OH⁻) or Carbamate (MEA)

Two materials that are selective for CO_2 are sodium hydroxide (NaOH or lye) and monoethanolamine (MEA), a basic chemical used to capture CO_2 from natural gas or flue gas. Both NaOH and MEA form basic solutions when dissolved in water. NaOH is the base used in the DAC example in Chapter 2 and MEA is used in the PCC example. This Box presents the relevant chemistry for both processes, and compares them to illustrate why stronger bases such as NaOH, may be preferred for air capture.
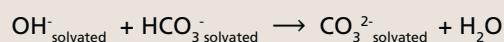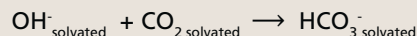
Solution Chemistry

Sodium hydroxide (NaOH) is a strong base, i.e. it dissociates completely into solvated sodium and hydroxide ions in water. One mole of NaOH dissolved in enough water for form a liter of solution is 1 molar in OH^- anion. The OH^- will participate in the equilibrium for the dissociation of water where water dissociates into hydroxyl and hydronium (water solvated hydrogen cation) ions. Water is amphoteric (it can act as an acid or a base): $H_2O \rightleftharpoons H^+_{solvated} + OH^-_{solvated}$, and this disassociation reaction has an equilibrium constant (K_{eq}) of 1.8×10^{-16} moles/liter at room temperature. Since 1 liter of water contains 55.6 moles of H_2O, for pure water the $H^+_{solvated}$ and $OH^-_{solvated}$ concentrations will be $\sim 1 \times 10^{-7}$ moles/liter. The pH of a solution is defined as the negative log of the $H^+_{solvated}$ concentration in moles/liter. Thus, the pH of pure water is 7. By introducing 1 M $OH^-_{solvated}$ via NaOH, the $H^+_{solvated}$ concentration drops to 1×10^{-14} moles per liter, or a pH of 14, to maintain equilibrium.

When the base MEA (monoethanolamine, or $NH_2CH_2CH_2OH$) is introduced into water, it reacts with the water in an acid-base reaction to generate $OH^-_{solvated}$, which increases the pH. The nitrogen in the MEA reacts with water to extract a proton to form a four-coordinate nitrogen with a positive charge: $NH_2CH_2CH_2OH + H_2O \rightleftharpoons {}^+NH_3CH_2CH_2OH_{solvated} + OH^-_{solvated}$. However, MEA is a weak base relative to NaOH, and the reaction does not proceed completely to the right, as it does for NaOH. The pH of a 1M MEA solution is about 11.7, which implies an $OH^-_{solvated}$ concentration of ~ 0.005M. Therefore when one mole of MEA is added to water, about 99.5% of the MEA will be present as solvated MEA, with only 0.5% present as the protonated ammonium ion form

Reaction of CO_2 with the basic solutions

The introduction of CO_2 into either the NaOH or MEA solution will result in acid-base reactions. A series of reactions involving the CO_2, water, and the base occur. Consider what happens when one adds CO_2 to 1M NaOH. Initially, two consecutive reactions take place:

$$OH^-_{solvated} + CO_{2\,solvated} \longrightarrow HCO^-_{3\,solvated}$$

$$OH^-_{solvated} + HCO^-_{3\,solvated} \longrightarrow CO^{2-}_{3\,solvated} + H_2O$$

which summed together gives:

$$2OH^-_{solvated} + CO_{2\,solvated} \longrightarrow CO^{2-}_{3\,solvated} + H_2O$$
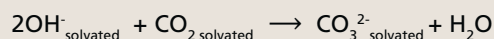
where the large excess of $OH^-_{solvated}$ in the 1M solution drives the reactions to the right. As long as hydroxide remains in excess, the H_2CO_3 will be driven toward carbonate.

As one keeps adding CO_2, eventually all of the hydroxide is consumed. Carbonate, now the most prevalent base in solution, continues to react with CO_2 and H_2O (or H_2CO_3) to produce bicarbonate:

$$H_2O + CO_{2\,solvated} + CO^{2-}_{3\,solvated} \rightleftharpoons 2HCO^-_{3\,solvated}$$
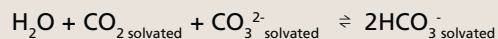
As increased quantities of CO_2 are absorbed into the 1M NaOH solution, the pH drops as the hydroxide ion is consumed and first carbonate buffer solution and then bicarbonate buffer solution forms. The pHs of the carbonate and bicarbonate buffers are at ~11.5 and ~8.5, respectively.

Box 3.3 Two Capture Chemistries: Carbonate (OH⁻) or Carbamate (MEA), cont'd

In the MEA solution, the CO_2 introduced into the solution can react directly with the basic nitrogen on the MEA molecule to form a molecule that rearranges to a molecule that is part cation and part anion, an electrically neutral molecule known as a zwitterion:

$$CO_{2\,solvated} + NH_2CH_2CH_2OH_{solvated} \rightleftharpoons {}^-OOCN^+H_2CH_2CH_2OH_{solvated}$$
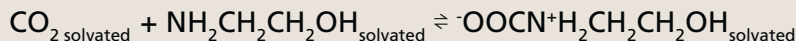
If the MEA were in large excess, the equilibrium will be driven to the right, and a second equivalent of MEA will react with the zwitterion to form an ion pair by accepting a proton from the zwitterion:

$${}^-OOCN^+H_2CH_2CH_2OH_{solvated} + NH_2CH_2CH_2OH_{solvated} \rightleftharpoons$$
$${}^-OOCNHCH_2CH_2OH_{solvated} + {}^+NH_3CH_2CH_2OH_{solvated}$$

The overall reaction of CO_2 with excess MEA produces a carbamate anion (an ion with a carbon atom bound to two oxygen atoms and a nitrogen atom) and an alkyl ammonium cation:

$$CO_{2\,solvated} + 2NH_2CH_2CH_2OH_{solvated} \rightleftharpoons {}^-OOCNHCH_2CH_2OH_{solvated} + {}^+NH_3CH_2CH_2OH_{solvated}$$

As this reaction proceeds and uses up some of the MEA, the pH of the solution decreases, because the MEA reaction with water ($NH_2CH_2CH_2OH + H_2O \rightleftharpoons {}^+NH_3CH_2CH_2OH_{solvated} + OH^-_{solvated}$) shifts to the left as the MEA is consumed, decreasing the concentration of $OH^-_{solvated}$. (This description is oversimplified, as reactions between OH- and CO_2, similar to those described above for the NaOH case but neglected here, are also taking place. All of the species equilibrate with one another.)

Stronger base is more effective for reaction with CO_2

The reactions of the 1M NaOH and 1M MEA solutions with CO_2 will be efficient and effective as long as the solutions remain basic enough to prevent the escape of CO_2 that arises from the decomposition of H_2CO_3, i.e., from the reversal of the route from dissolved CO_2 to form H_2CO_3 in aqueous solution. The reaction of a 1M NaOH solution with 0.5 equivalents of CO_2 results in a strongly basic carbonate solution, and reaction with a full equivalent of CO_2 results in the mildly basic bicarbonate solution. Under both conditions, with 0.5 or 1 equivalent of CO_2, the 1M NaOH solution will be efficient in CO_2 capture. On the other hand, the products from the reaction of 0.5 equivalents of CO_2 with a 1M MEA solution are a mild-base carbamate anion and a mildly acidic ammonium cation. Thus, further uptake of CO_2 should lead to a more reversible exchange of CO_2 between solution and gas and less effective capture. Taking into account only the binding step, not the subseq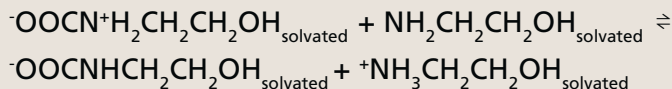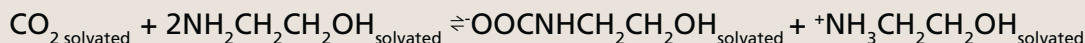uent release of CO_2, the NaOH solutions may be preferred over the MEA solutions for DAC, as they would have a larger capacity where up to one mole of CO_2 could be efficiently bound per mole of OH-, whereas only up to a half mole of CO_2 could be efficiently bound per mole of MEA.

These thermodynamic parameters determine the relative stability of the reactants (B and CO_2) and products (BCO_2), but do not determine the rate of binding once B and CO_2 are in close proximity, called the reaction kinetics. If the rate of the reaction were slow, it would limit the rate of the entire binding process. While it is important that the chemical reaction is fast, in the systems for PCC and DAC discussed in Chapter 2 the reaction rate is significantly faster than the rate of mass transfer across the gas-liquid interface. A discussion of these rates is presented in Appendix 3B [61, 62].

Alternative Materials for CO_2 Binding

Novel materials for binding CO_2 have begun to appear. Typically, these materials have been targeted initially for application in PCC, but they may also have promise in DAC systems. Many of these materials can be classified as emerging materials, and have only been assessed at the bench-scale. There are numerous outstanding questions about their utility, specifically concerning their performance under realistic conditions. The more developed materials technologies are being tested at the pilot-scale as alternatives to MEA for use in CO_2-absorbing solutions in PCC. Some of these promising materials are so-called "hindered amines," which have a lower CO_2-binding energy than MEA and thus lower energy requirements for regeneration [63]. Another option being explored is chilled ammonia solution, now being demonstrated for PCC [64].

Another liquid-phase approach, which is being investigated at the bench-scale and shown to be effective for CO_2 capture, is to use ionic liquids, salts that are liquid at ambient and process conditions. Initial research has found that ionic liquids are effective for CO_2 capture and they have the added benefit of low vapor pressure, which limits absorbent losses. Although ionic liquids are also non-flammable and environmentally relatively benign, mass production of these liquids is expected to be costly and difficult to scale up. Ionic liquids are quite viscous, making the transfer of CO_2 from the gas phase more difficult. However, this viscosity challenge has been addressed recently by redistributing the charge in the molecule to minimize the intermolecular forces between the ionic liquid molecules [65]. Recently, it was shown that by tethering the amine functionalities to the ionic liquid anion, only one amine function is required to complex one CO_2 molecule instead of the two required for most amines, where one amine center binds the CO_2 to form a carbamate anion and the second amine center accepts the proton to form an amine cation [66]. This high loading capacity suggests significant promise for ionic liquids if their other challenges can be overcome.

There is considerable interest in using solid adsorbents for capture of CO_2 from air. A 1969 patent proposed a scheme to capture the excess CO_2 in the air in a submarine [67]. It reported that over 99% of the CO_2 in the air could be captured in a strong-base ion exchange resin, that the CO_2 could be released by treating the resin with steam for a time at 100 ° C, and that the resin could be dried and recycled to capture more CO_2 with no apparent loss of capacity. However, the energy required to generate the excess of steam needed to release the CO_2 in the patent example was significant. This approach would not be sensible for DAC if the energy source to generate the excess of steam required were natural gas (or marine diesel fuel), because the CO_2 emissions associated with burning the fuel in this patent example are more than ten times the CO_2 captured from the air.

Recently, CO_2 capture schemes based on ion exchange resins and other solid sorbents have begun to be developed, some of which are specifically targeted to DAC [51]. One system uses ion exchange resins composed of a polymer backbone functionalized with organic ammonium cations which have adjacent anions ("counter ions") to achieve charge balance. These resins with OH^- as the anion that binds to CO_2 are currently being tested for air capture of CO_2 [51]. It has also been proposed that carbon capture, though not specifically DAC, can be performed with polymers that are functionalized instead with amines or branched organic molecules that have multiple amine sites along the branches. The use of appended molecules with more than one amine site allows chemistry similar to MEA to take place, where two amine centers are involved with the capture of one CO_2 molecule (see Box 3.3) [68].

Instead of a polymer support, the support could be a high-surface-area metal oxide, in particular silica. The use of metal-oxide supports may allow regeneration to be accomplished over a wider temperature range than polymer supports, and may also allow better control of the microporous structure to minimize the presence of adsorbed water. Silica has been functionalized with quaternary ammonium, amine, and polyamine sites [69]. Polymerized amines have been anchored to aluminosilicates, resulting in solids with amine site loadings and CO_2 binding potential two or more times higher than found in ion exchange resins [70]. Moreover, a metal-oxide support may be given some of the characteristics of a base, so that it donates electron density to the grafted basic centers, potentially enhancing the adsorption of CO_2 [68].

Christopher Jones and his group at Georgia Tech are developing solid sorbent materials that are alternatives to functionalized or grafted structures. This technology is considered a hybrid approach, where solid CO_2-selective sorbent particles are embedded within the porous matrix in the exterior section of a hollow fiber. The hollow fibers developed by Jones et al. do not act as membranes. The flue gas is passing on the exterior of these materials, and the CO_2 from the flue gas is trapped through adsorption in particles within the organic matrix on the exterior of the fibers. The organic matrix of the hollow fiber is porous, with the sorbent particles minimally attached to the pore surface in order to maximize their CO_2 interaction. The central hollow channel is isolated from the outside sheath and carries water to remove heat during CO_2 adsorption and steam during CO_2 release. Additionally, the way in which the hollow fibers may be aligned in a module for application may assist in minimizing CO_2 compression costs since the CO_2 upon desorption would be relatively confined [71].

Another potential solid adsorbent for DAC could be chemically functionalized activated carbon, which is being investigated for PCC. Activated carbons were first connected with the term adsorption by Heinrich Kayser in 1881. With their high surface area (up to 1500 m^2/gram) and tunable porosity and functionality, activated carbons serve as ideal, reasonable cost sorbents for condensable vapors in many applications. Current studies are focusing on enhancing the chemical reactivity and selectivity of activated carbon toward CO_2 through amine functionalization [72, 73].

Concentration Impacts

Regardless of whether the basic binding molecules are dispersed in a liquid medium or attached to a solid surface, both the strength and concentration of reactive molecules determines how effectively CO_2 will be removed from the input gas mixture. Concentration affects equilibrium directly, as seen in the reactions in Box 3.3. As the concentration of free, uncomplexed base (B) increases, the equilibrium is driven further toward the formation of the BCO_2 complex.

In addition to the direct concentration effect, increased concentration of basic sites on solid supports can lead to cooperative effects that can increase binding. For instance, the oxygen atoms in the CO_2 molecule have higher electron density after the carbon binds to a base to form the BCO_2 adduct. As a result, these oxygen atoms are more reactive and may interact with the support surface or a nearby water molecule to further stabilize the BCO_2 complex. As another example of a synergistic effect associated with basic site concentration, consider the formation of HCO_3^- from CO_2 bound to an OH^- counter anion associated with a tetra-alkylammonium cation tethered to a solid. If the binding site loading is high enough to create sites in close proximity, the OH^- ion associated with a second, adjacent tetra-alkylammonium cation can react with the HCO_3^- ion to form carbonate ion, CO_3^{2-}. Similar concentration effects may be observed with amine-functionalized supports via the formation of carbamate ion, alkyl-ammonium cation pairs. These supplementary stabilizations must be reversed during regeneration of the sorbent material, along with breaking the B-CO_2 interaction.

Binding-Site Poisons

As CO_2 is a weak acid, even PCC with 10% or more CO_2 in the flue gas requires the use of a fairly strong base, such as MEA, to remove the CO_2. With much lower concentration of CO_2 in air, even stronger bases, such as NaOH, may be preferred for DAC. However, if the feed gas contains molecules that are stronger acids than CO_2, they will react with the basic sites, acting as poisons to decrease the CO_2 binding capacity. Examples of gases in the atmosphere that bind to bases in preference to CO_2 include sulfur oxides (SO_x) and nitrogen oxides (NO_x)), which form acid rain, and despite intense scrubbing of acid gases from flue gas prior to PCC, a small amount of MEA will be tied up with breakthrough SO_x and NO_x. The resulting salt products are so stable that they are not decomposed in the regenerator. MEA can be regenerated from such salts only by isolating the salt product and treating it with OH^-, which, being a stronger base than MEA, displaces the NO_x or SO_x in an exchange reaction.

For DAC, if OH^- were the base used for capture, the presence of trace NO_x and SO_x in the air will consume some of the NaOH base to form salts. The total consumption of OH^- will be low because of the low concentration of NO_x and SO_x compounds in air (ppb in non-polluted areas), though the amount will vary depending on the air pollution at the capture site (up to 1 ppm in heavily polluted urban areas). If these salts form over time, they may build up in absorbent solutions, in which case some make-up solution will be required. If a solid sorbent were used, the acid gases may poison the sites irreversibly, and over hundreds of cycles steadily reducing the activity and effectiveness of the solid sorbent eventually require its replacement (refer to Box 3.1).

Binding-Site "Blocking"

Whereas a stronger acid than CO_2 may react with a basic capture site irreversibly and prevent further use of that site for CO_2 binding, an acid weaker than CO_2 can also create complications by interacting reversibly with the binding site, reducing the ability of CO_2 to bind to the site at a given moment. If the weaker acid is present in a significantly higher concentration than CO_2, the sheer number of its molecules present can block the CO_2 from binding effectively a large fraction of the time, thereby slowing down the observed rate of CO_2 binding. In particular, water can have this kinetic effect. Water is an amphoteric molecule (it can act as an acid or a base), and if the concentration of water greatly exceeds the concentration of the basic sites, water acting as an acid can slow down the reaction of the base with CO_2.

However, a water presence can have a synergistic effect in binding CO_2. The adsorption capacity of dry solids, absent of H_2O and OH^-, is lower than solids that contain some water on the surface or in the pores. Consider a solid that is functionalized with amine groups which may be used to capture CO_2. CO_2 first reacts with the amine to form a zwitterion with a negative charge on the oxygen in the CO_2 and a positive charge on the amine nitrogen, and later a free base deprotonates the zwitterion to form a carbamate anion. Under humid conditions, the water present can react with the amines to form OH^- and an ammonium cation. The OH^- may then react with CO_2 to form bicarbonate ion. In the limit, up to 1 mole of CO_2 may be captured per mole of amine sites. However, under completely dry conditions, the amine is the only available base and both a carbamate ion and ammonium ion form. As a result, 0.5 mole CO_2 is bound per mole of amine sites. Thus, while an excess of water vapor will interact with the basic sites, slowing the binding of CO_2, water may be necessary to maximize the adsorption capacity [68].

In an aqueous solution containing 30% MEA by weight (5.3 M) as might be used in a PCC process, there are approximately eight water molecules for every MEA molecule. A small portion of the MEA reacts with water to form OH$^-$ (see Box 3.3), and also the nitrogen atoms of unreacted MEA form hydrogen bonds with water. However a 30% MEA solution is effective for capturing CO$_2$ at the concentrations found in flue gas, and the interference, or "blocking" effect of water does not slow the CO$_2$ capture rate significantly. Moreover, the water serves the useful purpose of absorbing the heat of reaction of the CO$_2$ with the MEA.

One proposed DAC approach is to use a polymer-based ion exchange resin in the OH$^-$ form to capture CO$_2$ from the air. The OH$^-$ will be solvated by the water molecules in the micropores. An "as received" polymer ion exchange resin has 30-50% water content by weight. In air, the resin adsorbs or loses water, depending on the absolute humidity of the air. The OH$^-$ on the solid support is associated with a quaternary ammonium cation bound to the resin, and will be solvated by surrounding water molecules. The observed rate of CO$_2$ uptake is slowed by increased water presence in the micropores [55].

Among the step 4 questions/challenges are:

- Can CO$_2$ sorbents be identified that reduce the CO$_2$ binding strength and/or reduce the increase in order (reduce entropy loss) but remain effective at air capture, and thereby reduce the energy requirement for regeneration and CO$_2$ release?

- Can solid CO$_2$ sorbents be developed that have a greater number of accessible binding sites per unit volume and/or weight?

- Can high-surface-area solid CO$_2$ sorbents be developed with increased effectiveness in the presence of water? Might this be accomplished by minimizing water condensation in the pores to reduce the binding-site blocking effect of water? Or, alternatively, by taking advantage of the high water concentration to increase the effectiveness of CO$_2$ binding or absorb the heat released from the binding reaction?

- Can CO$_2$ sorbents be developed with reduced reactivity with NO$_x$ and SO$_x$ relative to CO$_2$ for placing of DAC in populated areas?

3.3 Release of CO$_2$

Once CO$_2$ is captured, it needs to be recovered in a concentrated form to prepare for sequestration. The final three of the seven steps involve the process of CO$_2$ release and recovery. In Step 5, the CO$_2$ is released from the sorbent material. In Step 6, the sorbent returns to a state where it is ready to capture CO$_2$ in the next cycle. In Step 7, the recovered CO$_2$ is "polished" to remove unwanted components released in Step 5, such as water, because a water-free CO$_2$ stream is required to prevent pipe corrosion during transport and sequestration. Step 7 also includes compression of the CO$_2$.

Step 5: Release of CO$_2$ from the binding site

Before CO$_2$ is released from the binding site, the medium containing the BCO$_2$ complex has to be isolated to allow the CO$_2$ to be recovered. Any constituents of the environment into which CO$_2$ is released must be able to be easily separated from the CO$_2$. CO$_2$ can be released into steam, for example, because CO$_2$ and water vapor can be separated easily by condensing the water. In PCC, the CO$_2$-rich MEA solution collects at the bottom of the absorption column and is pre-heated and transferred to the top of a separate desorption column. Steam introduced at the bottom of the desorption column heats the MEA solution, which leads to decomposition of just over half of the BCO$_2$ complex. The effluent vapor stream is cooled and then compressed to condense the water and produce a concentrated CO$_2$ stream. Further treatment of the CO$_2$ stream with a solid adsorbent, like a desiccant, may take place to reduce the water vapor content below 500 ppm for transport and sequestration.

For the DAC system described in Chapter 2, the isolation of the BCO$_2$ complex—in this case, sodium carbonate [Na$_2$CO$_3$]—is not straightforward, because the sodium carbonate remains soluble in the aqueous solution. Isolation of the CO$_2$ is accomplished by synthesizing calcium carbonate [CaCO$_3$], via an exchange reaction of sodium carbonate with calcium hydroxide [Ca(OH)$_2$]. Calcium carbonate precipitates from the solution and is recovered by filtration.

One benefit of using a functionalized solid support for air capture is that the support isolates the BCO_2 complex by attachment to the solid. The solid with bound CO_2 is then evacuated in a closed chamber to remove the air in the void space prior to release of the CO_2. However, chamber evacuation may not be straightforward, since the air must be able to be removed without release of the bound CO_2.

Thermal release of CO_2

Just as heat is released when CO_2 binds to a base, heat must be added to reverse the reaction and release CO_2 to recover the base. In the situation where the initial reactants (the base, B, and CO_2) are also the products, the principle of microscopic reversibility asserts that the heat required for unbinding will be the same as the heat released when BCO_2 is formed. In the DAC example from Chapter 2, solid $CaCO_3$ is the material that releases CO_2. In this instance, the release reaction is not simply the reverse of the adsorption reaction, as the CO_2 capture occurred in an aqueous NaOH solution. Heat must be provided to decompose solid $CaCO_3$ into CaO and CO_2. However, simply providing the heat of reaction will not be enough for the reaction to proceed. It must be provided at a sufficiently high temperature to drive the equilibrium of the reaction in the direction of decomposition. A significant activation-energy barrier must also be overcome to allow the reaction to proceed at a reasonable rate. As a result, the $CaCO_3$ must be heated to over 900° C for the decomposition to proceed rapidly. The heat needed to overcome the activation barrier may be partially recovered and put to good use, e.g., to dry the $CaCO_3$ precipitate. However, significant heat will be lost to the surroundings.

In PCC processes or in new processes that might be developed in the future for DAC, CO_2 release may occur by simply heating the CO_2-rich solution to break the bond between the base, B, and CO_2. However, because of the presence of "spectator molecules," such as the water in an MEA solution for PCC processes, the thermal costs associated with the decomposition of the adduct is not simply equal to the reverse of the heat released by the adduct formation. When MEA reacts with CO_2, the heat released is absorbed by the water molecules in solution and when the CO_2 is released, not only must heat be provided to decompose the carbamate molecule formed from the reaction of CO_2 and MEA, but heat will also be required to raise the temperature of the water in the solution to the point where the reaction equilibrium is reversed and fast release of the CO_2 can take place. Although some of the heat absorbed by the water solvent can be recovered from the "lean" MEA solution as it is returned to the absorber column, a significant amount of heat will be wasted through transfer to the surrounding environment (see Box 3.4).

Box 3.4   Energy Requirements and Thermal Losses for Releasing CO$_2$ from a 30% MEA Solution

The use of MEA for post combustion capture of CO$_2$ involves the circulation of the MEA solution between the absorber column and the regeneration (stripper) column where CO$_2$ is released.   The MEA solution that enters the absorber is the "lean" solution and the MEA solution entering the regeneration column is the "rich" solution. Not all of the CO$_2$ is released in the stripper column, which operates between ~100°C and 140°C. For example, a lean 30% MEA solution may retain a loading of ~0.2 moles of CO$_2$ per mole of MEA, whereas the rich solution contains ~0.4 moles of CO$_2$ per mole of MEA[9].

The heat of reaction (ΔH) of CO$_2$ with a 30% MEA solution at 40°C (approximate temperature of the absorber column) is -84.3 kJ/mole of CO$_2$ [74]. Using this value as the amount of heat needed to decompose the CO$_2$-MEA adduct, each cycle requires ~16.9 kJ per mole of MEA to release 0.2 moles of CO$_2$. However this energy requirement is only part of the energy needed in the stripper.

The heat capacity of a 30% MEA solution with 0.4 moles of CO$_2$ bound per mole of MEA has been measured as 3.418 J/gm-K [75].The mass of the solution containing one mole of MEA also includes the 0.4 moles of CO$_2$ as well as 7.9 moles of H$_2$O, resulting in a total of 221 grams per mole of MEA. Therefore, 756 J are required to heat the 1 mole of MEA in solution 1 degree. Assuming the absorber column operates at 40°C and the stripper column at 120°C, the heat required to heat the 1 mole MEA in solution is ~60.5 kJ. This requirement to heat up the solution is about 3.5 times the energy needed to release the 0.2 moles of CO$_2$ per mole of MEA. Of the 60.5 kJ, nearly 80% is needed to heat up the water.

While significant heat can be recovered from heating the MEA solution, for example by heat exchange between the hot lean solution leaving the stripper column and the cooler rich solution entering the stripper, thermal losses of 10% or more can be anticipated. While the enthalpy to release the CO$_2$ is ~16.9 kJ per mole of MEA in solution, the thermal losses associated with the MEA solution cycle will be at least 6 kJ, or 35% of the heat required to release the CO$_2$.

The same issue will arise for direct air capture if the release of the CO$_2$ involves heating "spectator molecules" such as water. Heat will have to be expended to heat up and potentially vaporize these molecules along with the BCO$_2$ complex itself.   In the Chapter 2 air capture example, the amount of water in the CaCO$_3$ precipitate will need to be minimized prior to the calcination step. For high surface area solid sorbents using thermal CO$_2$ release and regeneration, both the support material and the water content in the pores will consume valuable energy during the heating cycle.

An additional consideration for the decomposition of the BCO$_2$ complex is the thermal and chemical stability of the sorbent base, B. Especially if the sorbent is an organic molecule, the heat added to release CO$_2$ could lead to thermal decomposition. In addition, during the desorption step, a sorbent may be oxidized by oxygen carried over from the absorption step or decomposed by reaction with the water (hydrolysis) that may be present.   These reactions result in some loss of the sorbent, and this degradation process over time will result in a requirement to replace some or all of the sorbent. These processes occur for PCC that uses MEA as a solvent, and as a result, 1-2 kg of MEA must be replaced for every ton of CO$_2$ captured. Over the course of a year, the replacement additions become multiples of the original quantity of MEA present.

These degradation pathways may be expected in air capture involving organic bases such as amines in solution, solid functionalized organic polymers, or organic bases anchored to solid metal-oxide supports. Adding make-up absorption solution in a continuous fashion is relatively straightforward from a process point of view. However, full replacement of structured solid sorbents will have to be carried out periodically depending upon the rate of loss of binding sites with each adsorption/desorption cycle.

Release of CO$_2$ by displacement with another molecule

The previous section described a proposed scheme for CO$_2$ capture using a polymer-based ion exchange resin in the OH- form and indicated that competition from water in the pores interacting with the OH- anion slows the observed rate of CO$_2$ binding. The same water-CO$_2$ competition, however, is a potential route to release of the captured CO$_2$ by flooding the pores of the resin with water. The process may be accomplished either by submerging the resin in water or by treating the resin with warm water vapor after the void space around the resin has been evacuated. The

increased water concentration results in the solvation of the OH- and the release of CO_2 molecules from the binding site. In this case water (the weaker acid) displaces some of the CO_2 (the stronger acid) simply through a concentration effect. The released CO_2 will be saturated with water vapor, and the resin will be saturated with liquid water. The thermal energy required for CO_2 release and regeneration is thereby broken into multiple steps—warming the water or water vapor for the CO_2 displacement reaction, and subsequent thermal energy use to remove the water from the CO_2 effluent and excess water from the pores of the ion exchange resin.

The water vapor in this example helps displace the CO_2 and then sweep the CO_2 away from the base site, preventing re-binding. In this example, water serves two roles by displacing the CO_2 and carrying it away. This case is distinct from a situation where an inert gas simply sweeps away a small amount of desorbed CO_2 and continues to sweep away the CO_2 as it desorbs. The approach using an inert sweep gas results in a very large excess of sweep gas in the effluent relative to the amount of CO_2 [76].

Among the step 5 questions/challenges are:

- In air capture systems where a second material (e.g., $CaCO_3$) is required to concentrate the CO_2-carrying entity prior to CO_2 release, can materials be developed that lower the temperature of CO_2 release?

- Can catalysts be developed to reduce the activation energy and lower the temperatures needed for CO_2-release processes?

- Can liquid absorbents be designed that reduce or eliminate evaporative or carry-over losses that may occur, especially during the CO_2 desorption step?

- Can organic liquid absorbents or organic functionalized CO_2-capture adsorbents be developed with increased resistance to oxidation and hydrolysis and/or with improved thermal stability during CO_2 release?

- When displacement by another molecule is used for CO_2 release, can lower-volatility molecules be developed which result in CO_2 being a larger fraction of the effluent, and/or which require less energy to regenerate the sorbent than when using water?

Step 6: Regeneration of the binding material and/or medium

In the PCC example in Chapter 2, the regeneration of the MEA solution occurs simultaneously with CO_2 release. The MEA solution is then cooled and returned to the absorber column. In the DAC example presented in Chapter 2, however, calcination decomposes the $CaCO_3$ to form CaO, and additional steps are required to regenerate the NaOH solution for return to the absorber. First, the CaO is hydrated to form $Ca(OH)_2$, and then the $Ca(OH)_2$ is reacted in a subsequent step with the Na_2CO_3 in the absorber effluent via an exchange reaction that regenerates the NaOH solution and precipitates $CaCO_3$. Little to no $Ca(OH)_2$ should end up in the NaOH solution, because $Ca(OH)_2$ would react with CO_2 in the absorber to form $CaCO_3$, which would precipitate in the absorber creating fouling and physical blockage.

In the case where the CO_2 is captured from air using an anion exchange resin and is released using warm water vapor, regeneration of the resin requires considerable energy to evaporate the excess water. It has been proposed to let nature provide the energy for evaporation by arranging for the water to evaporate off the adsorbent resin into warm, dry ambient air, much like drying laundry in the wind [51]. The rate of water loss, and therefore rate of regeneration of the adsorbent, will depend on atmospheric temperature, wind speed, and relative humidity. Cold, damp conditions would retard the rate of, and possibly prevent, regeneration. In order to capture the energy cost savings, capture schemes with passive regeneration may be feasible only in locations with advantaged warm, dry weather conditions.

Among the step 6 questions/challenges are:

- Where an exchange reaction is required for solvent regeneration (e.g., the reaction of $Ca(OH)_2$ and Na_2CO_3 to regenerate NaOH and precipitate $CaCO_3$), can a process be developed such that the regenerated solvent is not contaminated with species that can lead to fouling of the absorber?

- Can air-capture modules using fixed sorbents be configured to take full advantage of thermal energy from the sun and from wind currents to increase the rate of regeneration?

Step 7: Concentration and compression of the CO_2

The capture processes considered in Chapter 2 produce CO_2 streams containing a significant amount of water vapor. To produce a sequestration-ready CO_2 stream, the water needs to be removed, because compressing CO_2 with water present produces a fluid that corrodes pipeline and well materials. Although most of the liquid water can be separated from the CO_2 by cooling and condensation, the CO_2 requires additional drying to bring water content below 500 ppm. The additional "polishing" process may involve passing the compressed CO_2 over a desiccant.

CO_2 needs to be compressed to approximately 100-150 atmospheres (10-15 MPa, or 1500-2200 psi) before it enters a pipeline for transport to a storage site. The pipeline pressure is set by the need for CO_2 to have a high density, which requires that it be in a supercritical state, i.e., that its pressure exceeds the critical pressure of CO_2, 73 atmospheres. The CO_2 pressure entering the compressor depends on the previously discussed CO_2 release processes. The energy required to compress the CO_2 to the pipeline transport pressure is related to the ratio of the outlet pressure of the gas sent to the pipeline to the inlet pressure from the CO_2 release process, and therefore is lower when the pressure of process effluent is higher. In the example where the CO_2 is recovered from the solid adsorbent by water vapor displacement in a pre-evacuated chamber, the effluent gas pressure will be sub-atmospheric: it is the sum of the partial pressure of water at the chamber temperature and the partial pressure of the CO_2 released (which, in turn, depends on the amount of CO_2 released and the chamber volume). The low pressure of the effluent increases the compression energy required, relative to a process that releases CO_2 at atmospheric or higher pressure.

For the DAC example presented in Chapter 2, natural gas is burned with oxygen to heat the calciner. A practical concern will be oxygen breakthrough into the water vapor/CO_2 effluent. An alternative approach may be to use air instead of oxygen as the oxidant for the combustion, in which case large volumes of nitrogen would accompany the CO_2 and water. The nitrogen would then need to be separated from the CO_2, in effect requiring a PCC cycle on the back end of the air capture process to recover the CO_2 at a purity suitable for sequestration.

Among the step 7 questions/challenges are:

- Can new CO_2 release processes be developed such that the pressure at which CO_2 is released is raised in order to reduce power consumption for subsequent compression to pipeline pressure?
- Can improved processes be developed to remove oxygen, water and/or other trace materials from the CO_2 streams that are otherwise detrimental to the transportation and sequestration process?

3.4 Integration

Improvements in any of the seven steps above may reduce the DAC cycle time, which in turn could improve capital utilization and reduce variable and fixed operating costs. However, all of these steps are linked, and a full integrated system solution will be required. Improvements in any one step are more than likely to lead to complications in another step, or reduce operating costs at the expense of increased capital requirements or vice versa. Advance in any step is likely to require reevaluation and redesign of other process steps. Over time, potential technical breakthroughs and the use of an iterative development process could result in demonstrated and scalable direct air capture processes.

Significant advancements or breakthroughs in PCC processes may be leveraged for DAC, and vice versa. On the other hand, DAC has its own set of unique challenges that may provide the need for technology development specific to this application.

Process integration can reduce costs by improving the use of both materials and heat. Integrating and balancing the through-cycle material flows in an air capture process should reduce materials losses. The integration of heat flows across process steps to minimize the production of waste heat should reduce the energy input requirements.

Ultimately the question is whether a full-cycle direct air capture process can be successfully demonstrated, and, subsequently, whether it can be shown to operate effectively and efficiently over hundreds to thousands of consecutive cycles.

Although the minimum work calculation reveals that, from a thermodynamic perspective, the energy required for DAC vs PCC will be a factor of three greater, optimization of both the DAC individual steps and the overall process may lead to some convergence in the costs of PCC and DAC relative to the eight-fold difference reported in Chapter 2. However, even with technical breakthroughs in DAC, the capture of CO_2 from more concentrated sources such as power plant flue gas will be significantly cost advantaged relative to air capture.

3.5 Features of the research frontier of Direct Air Capture of CO_2

Costs for DAC will not fall substantially through incremental improvements in present-day technology, as improvements in one process step may create additional challenges in other process steps or simply lead to trade-offs between capital and operating cost without reducing the cost of the overall process. A trade-off explored repeatedly in this report, for example, exchanges stronger, more efficient binding of CO_2 in the capture reaction for greater energy requirements for regeneration. Transformational changes will likely require the integration of achievements in several fields of materials science, as well as in chemical and process engineering.

"Proof of concept" experiments—bench experiments that run absorbents through numerous cycles—are the first step. As experimental regimes evolve, they may be supported by computational analysis. Pilot plants to study full integration and scale-up will be justified only when bench experiments indicate that effective, repeatable sorption-desorption schemes addressing the many challenges and opportunities described in this report have been delivered.

The PCC and DAC research frontiers have many common features. PCC researchers, motivated largely by the objective of reducing the costs of industrial CO_2 capture, are pursuing several novel chemical approaches to CO_2 separation that overlap the DAC frontier [77]. The evolving exploratory and fundamental research program could lead to new materials, such as sorbents and catalysts, with far superior properties relative to materials available today, such as metal-organic frameworks (MOFs) (See Box 3.5). These materials could perhaps leverage entropy changes throughout the process. A number of ongoing areas of research may provide leads to such materials, including research into high absorbent loading, enzymes, plastics, ionic liquids, membranes, adsorbents, innovative absorber configurations, integration of CO_2 capture with renewable energy, and new sorption-desorption cycles.

The DAC research frontier has its own unique challenges. Needed, for example, are sorbents with greatly enhanced properties for cycling CO_2, yet capable of being taken through thousands of sorption and desorption cycles with minimal degradation of performance and at moderate cost. One frontier is new binding chemistries, based on mimicry of aspects of photosynthesis or on inorganic chemical systems that have no analogs in biology. A second frontier of air capture is the search for improvements at the level of chemical engineering systems, where strategies very different from those used for industrial capture today can be imagined. Notably, solid adsorbents, where the sorbent is chemically bonded to a rigid substrate, may be more relevant to an open system like air capture rather than to industrial capture where closed systems are used. A third frontier is associated not with gas separation, but with the challenge of lowering the cost of transporting large volumes of air through the sorption unit.

Box 3.5. Metal-Organic Frameworks (MOFs) as an Example of Emerging Materials

New materials research is necessary to develop game-changing technologies for CO_2 capture. In the last few years, there has been a wide-ranging research effort, at the U.S. Department of Energy and elsewhere, to develop such new materials. The majority of these new materials are only now being developed and characterized and have not been investigated past the bench-scale. It is unclear whether they will have real-world applications for post-combustion or direct air capture, or for neither of these systems.
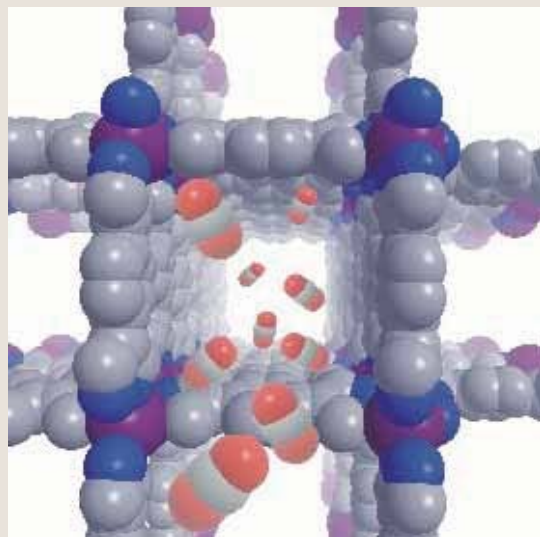
Fig. 3.B5.1. A metal-organic framework consisting of cobalt atoms (purple) linked by an organic bridging ligand (1,4-benzenedipyrazolate, with nitrogen and carbon atoms shown in blue and grey, respectively) and CO_2 molecules (red-grey-red spheres).

(Deanna M. D'Alessandro/UC Berkeley)

One example of emerging material for CO_2 capture is metal-organic frameworks (MOFs), a new class of nanoporous crystalline materials (Figure 3.B5.1). MOFs are composed of organic bridging ligands and are coordinated to metal-based nodes to form a three-dimensional extended network with uniform pore diameters typically in the range 3 to 20 Angstroms (Å). The nodes generally consist of one or more metal ions (e.g., Al^{3+}, Cr^{3+}, Cu^{2+}, or Zn^{2+}) to which the organic bridging ligands coordinate via a specific functional group (e.g., carboxylate, pyridyl). These materials have high thermal and chemical stabilities, unprecedented internal surface areas (up to 5000 m^2/g), high void volumes (55-90%) and low densities (from 0.21 to 1.00 g/cm^3) [78, 79]. Recent studies show that these materials can selectively adsorb CO_2 [31, 80-82]. Current research focuses on tailor-making MOFs, by varying the organic bridging ligands, the metal ions and binding sites, in order to tune the materials for desired adsorption and desorption behaviors. It is possible that one MOF would be developed that is good for a direct air capture process and another MOF would be developed for a post-combustion capture process. The same may be true for other flexible materials and processes, such as ionic liquids and the hollow-fibers developed by Lively et al. [71].

Because researchers are just now learning about their properties, a MOFs-based CO_2 capture process, either from air, flue gas or another gas mixture, cannot be built today, or even in the near-term. For example, the CO_2 adsorption by MOFs in the presence of water vapor is still unknown. Because of the high concentration of water in ambient air, this will be a vital consideration in developing MOFs, or any other material, for DAC. These materials are instead envisioned as a part of a CO_2 capture process that will be built in the future. Moreover, since these new materials are unlike the existing materials, such as MEA for PCC or NaOH for DAC, significant engineering advances will be needed to develop a full CO_2 capture process. This is particularly true because MOFs are currently extremely expensive. As the new materials are developed and characterized, both computationally and experimentally, the full range of their possible applications should be considered. Thus, new materials might be considered for post-combustion and direct air capture, but also for pre-combustion capture and capture for other processes like capture associated with natural-gas and oxy-fuel combustion.

Appendix 3A. Contactor Design for Air Capture

Capture rate for a given frontal area, velocity, and removal fraction

The CO_2 concentration in air can be expressed in many useful units. Rounding off the concentration, 400 out of every million molecules (400 ppm) in air are CO_2 molecules. Choose the density of air, ρ, to be 1.2 kg/m^3 (equivalently, 1.2 grams per liter) at 1 atmosphere and 25 °C, and choose 29 g/mol as the average molecular weight of air. Then, in a cubic meter of air there are 41.4 total moles of *all* molecules. Each cubic meter of air contains 0.0166 moles (one sixtieth of a mole) of CO_2, and each liter of air contains 1.66x10^{-5} moles of CO_2. (Moles here are always gram-moles, a number of grams equal to the molecular weight.) Finally, since the molecular weight of CO_2 is 44 g/mol, the mass of CO_2 per unit volume of air, C_o, is:

$$C_o = 0.72 \; gCO_2/m^3 \qquad\qquad\qquad\qquad (1)$$

When air flows through a contactor at a volume flow rate, Q [m^3/s], the rate at which CO_2 is removed from the atmosphere, $\dot{M}$ [kg/s], is:

$$\dot{M} = \alpha C_0 Q, \qquad\qquad\qquad\qquad (2)$$

where α is the fraction of the CO_2 in the flowing air that is removed by the contactor. Two important design parameters are the frontal area of the contactor, A, and the velocity, U, of the air flowing through the contactor. The air flow rate through the contactor is:

$$Q = UA, \qquad\qquad\qquad\qquad (3)$$

and the rate of CO_2 capture from the air is:

$$\dot{M} = \alpha C_0 UA \qquad\qquad\qquad\qquad (4)$$

The rate of capture divided by the frontal area is the *capture flux, $\alpha C_o U$*. Choosing as inputs to Equation (4), for example, U = 2 m/s (nearly 5 mph) and α = 0.50. the capture flux is 0.72 g CO_2/ m^2-s. In other units this flux is 62 kg CO_2/ m^2-day and 22 tCO_2/m^2-yr.

The per capita CO_2 emissions rate for Americans is about 20 tons/yr. Therefore, matched to the average American's emissions is a contactor with an effective frontal area of one square meter through which air flows at about 5 mph air while 50% of the CO_2 in the air is captured.

Thickness of the contactor and fraction captured

Another important parameter in contactor design is the fraction of CO_2 removed from a gas mixture. The fraction captured can be increased by moving the CO_2 through any system more slowly, but with poorer use of capital. A denser loading of sorption sites can increase CO_2 uptake, perhaps resulting in heat removal problems and shortened sorbent lifetime. A more strongly binding sorbent can be used, but in exchange for greater energy expenditure during regeneration. No matter how these choices are made, the fraction captured can be increased by making the contactor thicker (for horizontal flow) or higher (for vertical flow), increasing the capital cost.

The issue of contactor thickness is illustrated in Figure 3A.1. The unit rectangle represents a contactor capturing 50% of the incident CO_2, and two ways of using two identical contactors are sketched. In (a), the second contactor is placed alongside the first and, relative to the single contactor, twice as much air enters the system and twice as much CO_2 is removed. In (b), the second contactor is placed behind the first, the same amount of air enters the two-contactor system as enters the single contactor, and three-quarters of the incident CO_2 is removed, i.e., 1.5 times as much CO_2 as from a single contactor. If the cost of the capture system is driven by the cost of the contactor, both two-contactor systems will cost about the same, and the side-by-side system will be cheaper, per ton of CO_2 captured. In essence, thinner is cheaper—when the dominant cost is the cost of the contactor and there is a nearly infinite supply of feedstock air. To be sure, there are situations where side-by-side will not be cheaper; for example, a facility that extends a long distance across the countryside may require more pumping of fluids and may be a more disruptive presence (generating greater community resistance) than a facility with a compact design.

This example shows immediately that the fraction not captured falls exponentially with the thickness of the contactor. There is a characteristic length for this exponential behavior, as will be discusses discussed in the next section.

Figure 3A.1. A thick vs. a thin contactor
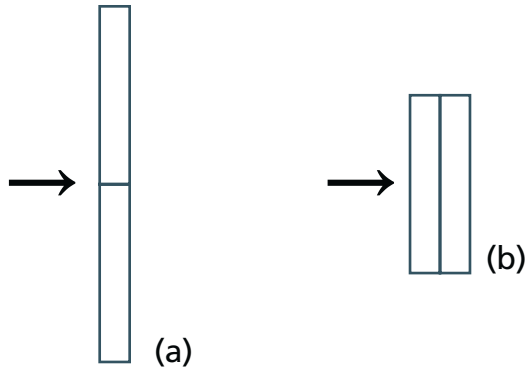
Pressure drop and fan power

Imagine that the contactor consists of long, narrow, cylindrical horizontal channels arranged in parallel like a honeycomb and that, as air flows through a channel, CO_2 is captured by a sorbent lining the inside of the channel. For the rest of this Appendix, the focus is on a single channel.

Assume that as the air flows through a channel, its pressure falls by P_{drop} [Pa, or J/m³]. The power per unit time required to move the air, $\dot{E}$ [J/s], often provided by fans, is:

$$\dot{E} = P_{drop}Q, \tag{5}$$

neglecting any change in the air velocity. Dividing Equation (5) by Equation (2), the energy required per unit mass of CO_2 removed is:

$$\dot{E}/\dot{M} = P_{drop}/(\alpha C_o) \tag{6}.$$

Consider, as inputs to Equation (6), a pressure drop of 100 Pascals (Pa) and a 50% capture rate. The result is 278 kJ/kgCO_2.

If all the energy to move the fluid were provided by electric fans, with 80% system efficiency, it would take 347 kJ of electricity to capture 1 kgCO_2, or 96 kWh to remove 1 tCO_2. (Note that 1 kWh = 3.6 MJ.) At 10 cents/kWh, the cost of the fan power would be about \$10/tCO_2.

One can see immediately that, for a 50% capture rate, pressure drops much in excess of 100 Pa will create severe cost pressure on CO_2 capture, given that capture costs below a few hundred dollars per ton of CO_2 are a typical target for air capture processes. Moreover, there is the "net-carbon" issue: How large are the CO_2 emissions associated with the fan power? If, for example, the electricity were provided by coal without CO_2 capture and storage at the coal plant, the carbon intensity of the electricity would be approximately 1000 gCO_2/kWh, and fan power on its own would contribute 100 kg CO_2 of emissions (one tenth of a ton) for each ton of CO_2 captured.

Pressure drop for laminar flow through narrow channels

Air flow at slow speeds within narrow channels produces laminar flow. Laminar flow, in contrast to turbulent flow, can be described with simple equations. Laminar flow through narrow channels is called Poiseuille Flow. The pressure drop for Poiseuille flow through a cylindrical channel of diameter d [m] and length L [m] is given by the equation:

$$P_{drop} = 32\rho vUL/d^2. \tag{7}$$

Here, v is the kinematic viscosity of air, 1.5×10^{-5} m²/s. The dimensionless Reynolds number, R_e, is defined in terms of the kinematic viscosity:

$$R_e = dU/v. \tag{8}$$

Equation (7) can be restated in terms of the Reynolds number:

$$P_{drop} = 32\rho \, U^2 L/R_e d, \qquad\qquad R_e < 2000. \tag{9}$$

Laminar flow can be expected until $R_e \approx 2000$, or, equivalently, for values of the product of d and U that are less than 0.03 m²/s. For U = 2 m/s, one should find the transition to turbulence at a channel diameter of about 1.5 cm.

From Equation (7), for a flow of 2 m/s and a channel diameter of 0.01 meters (1 centimeter), recalling that the density of air, ρ, is 1.2 kg/m³, the pressure drop per unit length, P_{drop}/L, is 11.6 Pa/m. It would take a 9-meter-long channel to produce a 100 Pa pressure drop. On the other hand, for the same velocity, if the channel diameter were 1 millimeter, a pressure drop of 100 Pa would occur in just 9 centimeters.

A long-enough channel

An important design constraint is that the channel is long enough for there to be time for the CO_2 to diffuse to the walls. The CO_2 in the flowing air will diffuse to the channel walls with a characteristic diffusivity, D [m²/s]. A result of the kinetic theory of gases is that the diffusivity and the kinematic viscosity, which describe momentum and mass transfer, respectively, will have similar values when the molecular weights of the diffusing gas and the gases through which it is diffusing are not very different. From (Hirschfelder et al., 1954 [83], Table 1.2-3, p. 16), using the value of the kinematic viscosity given above:

$$D \approx 2.1 \times 10^{-5} \, m^2/s. \tag{10}$$

It is customary to introduce the dimensionless Peclet number, P_e, which is the analog of the Reynolds number defined in Equation (8):

$$P_e = Ud/D, \tag{11}$$

and the Schmidt number, S_c, which is the dimensionless ratio:

$$S_c = v/D = P_e/R_e. \tag{12}$$

The Schmidt number for CO_2 in air is 0.72.

The CO_2 concentration in the channel is governed by a linear partial differential equation. When the air velocity profile is assumed to be independent of the axial coordinate, the problem can be solved by the method of separation of variables. As expected from the discussion related to Figure 3.A1.b above, the concentration falls exponentially as a function of the distance from the front end of the channel. The exponential relationship between the capture fraction, α, and the length of the channel, L, can be expressed algebraically as:

$$\alpha = 1 - exp(-L/Lo), \tag{13}$$

where

$$L_o = \eta Ud^2/D = \eta P_e d. \tag{14}$$

The parameter, η, is the dimensionless separation constant of the slowest decaying mode, which is the physically meaningful solution. Its numerical value depends on how effectively the CO_2 is removed at the channel wall.

L_o establishes the length scale for the problem. A long-enough channel would have a length of approximately L_o. Channels much shorter than L_o are probably too short, because the capture fraction will be substantially less than 1. Channels much longer than L_o are probably longer than necessary.

From Equation (14), for the same system and same capture fraction, a channel diameter 10 times narrower permits the use of a 100-times shorter channel. Countering the economic value of a smaller diameter, however, are the practical difficulties of cleaning small passages.

An interesting limiting condition for channel flow with diffusion and capture at the boundary assumes that the CO_2 removal process at the channel wall is ideally effective, meaning that uptake at the wall is so much faster than diffusion to the wall that the concentration at the inside surface of the channel is zero. A parabolic radial dependence for the air velocity in the channel is also assumed: $u(r) = 2U(1—4r^2/d^2)$, where r is the radial variable ($0 \le r \le d/2$) and U is the average velocity of the flow, first introduced in Equation (3). For this limiting case, the value of η is found numerically [84, 85]:

$$\eta = 0.068 \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (15)$$

When the removal process at the channel wall is less than ideal, the value of η is expected to be larger.

Using Equations (14) and (15), consider a flow velocity of 2 m/s and a channel with a diameter, d, of 0.01 m (one centimeter). Recalling that the diffusivity, D, is about 2.1×10^{-5} m²/s, the characteristic channel length for ideal capture at the walls is $L_o = 0.65$ meters. From Equation (13), 50% capture needs a 45-centimeter channel and 75% capture needs a 90 –centimeter channel.

Combining Equations (7), (12), and (14) yields another expression for the pressure drop:

$$P_{drop} = (32\eta S_e)\rho U^2(L/L_o), \qquad\qquad\qquad R_e < 2000 \qquad (16)$$

Returning to the discussion at Equation (6), the ratio of interest for contactor design is the energy required to move the air through the channels, per unit mass of CO_2 captured. Combining Equations (9), (13), and (14), this ratio is:

$$\dot{E}/\dot{M} \approx (32\rho U^2/C_o)(L/R_e d)/[1—exp(-L/\eta P_e d)], \qquad Re < 2000. \qquad (17)$$

Adding turbulence to the flow may be useful. Turbulent flow is more dissipative than laminar flow, which would increase the numerator in Equation (17), but it also improves delivery of the CO_2 to the sorbent, which would increase the denominator. In fact, contactors are usually deliberately designed to introduce a small amount of turbulence into the flow, trading greater pressure drop for better mass transfer.

Appendix 3B. Reaction Rates

The rate of the CO_2 binding reaction with a generic base molecule ($CO_2 + B \leftrightarrow BCO_2$) is

$$r_{CO2} = k_f[CO_2][B] - k_r[BCO_2]$$

where $[BCO_2]$, $[B]$ and $[CO_2]$ denote the molar concentration of BCO_2, B and CO_2, respectively, in mol/L and k_f and k_r are the rate constants for the forward and reverse reactions, respectively. When the first term dominates the sum and there is no replacement of CO_2 from outside the system, the CO_2 concentration decays exponentially with the rate constant, $k_f x[B]$.

Table 3B.1 shows published equilibrium constants, reaction enthalpies and rate constants for some of the reactions discussed in this report where B = H_2O, OH^- or MEA. Note that the rate constant and reaction enthalpy depends on factors such as temperature, pH and ion strength. For clarity, Table 3B.1 presents one representative value for the equilibrium constant and the rate constant. The second and third rows, corresponding to the two examples worked out in Chapter 2, are discussed below.

Table 3B.1. Published reaction enthalpies, rate and equilibrium constants for CO_2 binding reactions.

Reaction	Reaction Enthalpy (kJ/mole)	Equilibrium Constant	Rate Constant
[86]CO_2(aq) + $H_2O \rightleftharpoons H_2CO_3$	-19.5	[a]$K = 1.15x10^{-3}$	[a]$k_f = 4.68x10^{-2}$ s^{-1} $k_r = 40.65$ s^{-1}
[87]CO_2(aq) + $OH^- \rightleftharpoons HCO_3^-$	-109.4	[b]$K = 3.21x10^7$ M^{-1}	[b]$k_f = 1.24x10^4$ M^{-1} s^{-1} $k_r = 3.86x10^{-4}$ s^{-1}
[88]CO_2(aq) + $RNH_2 \rightleftharpoons RNHCOOH$	-60-90[d]	[c]$K = 4.9x10^2$ M^{-1}	[c]$k_f = 6.11x10^3$ M^{-1}s^{-1} $k_r = 2.98x10^1$ s^{-1}

References:

a. T = 30 deg C; Soli et al. [89]

b. T = 30 deg C; Pinsent et al. [90]

c. T = 30 deg C; McCann et al. [91]

d. Chowdhury et al. [92]

A. $CO_2 + OH^- \Leftrightarrow HCO_3^-$ (DAC Example in Chapter 2)

The forward reaction of CO_2 with hydroxyl (OH^-) is fast, with a rate constant of $1.24x10^4$ M^{-1}s^{-1}. (M means "moles per liter") The forward reaction rate is directly dependent on the concentration of (OH^-) and thus the reaction is proportionally faster at high pH.

B. $CO_2 + RNH_2 \Leftrightarrow RNHCOOH$ (PCC Example in Chapter 2)

The specific example shown in the Table, the reaction of CO_2 with MEA, has a forward rate constant ($k_f = 6.11x10^3$ M^{-1} s^{-1}) that is within a factor of two of the forward rate constant for the OH- reaction just considered. The reaction enthalpy for MEA, being less negative, is more favorable, from the perspective of the energy needed for regeneration. However, the equilibrium constant is less favorable, as the rate constant for the reverse reaction, $2.98x10^1$ s^{-1}, is 5 orders of magnitude greater than the reverse reaction with the OH^- system. As a result the MEA reaction does not go as completely to the right as the OH^- reaction at similar base concentrations.

In both instances, since the forward reaction dominates over the back reaction, the product of the forward rate constant and the concentration in air provides an estimate of the chemical reaction rate. Taking 10,000 M⁻¹s⁻¹ as a representative forward reaction rate constant and 1 M as the concentration of the binding agent, the exponential rate constant for CO_2 absorption is 10,000 s⁻¹, so that the characteristic time for absorption is 100 microseconds.
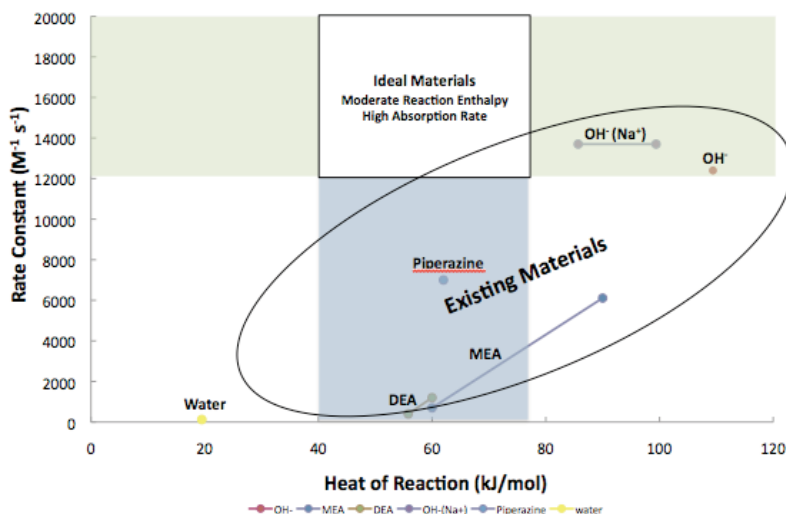
Figure 3B.1. Rate constant (liter/mol-sec) vs. absolute value of the reaction enthalpy (kJ/mol) for chemical sorbents.

Figure 3B.1, plots kinetic data versus thermodynamic data for several CO_2 reactions, including absorption processes using OH⁻ and MEA. When a range of values is available in the literature, several data points are plotted for the same binding material, thereby including some of the dependence of absorption rate on temperature, pH, and ion strength, and some of the dependence of the reaction enthalpy on all of these factors as well as CO_2 concentration. This plot clearly shows that for today's CO_2 capture technologies, absorption rates and reaction enthalpies are strongly positively correlated. The reason for this correlation is that all of the reactions are of the form $B+CO_2 \rightleftharpoons BCO_2$, and the entropy (DS) decreases as the reaction proceeds. Thus, if you consider two binding reactions, the *TDS* term is approximately the same and the difference in the spontaneity (ΔG) of reactions depends only on the difference in the reaction enthalpies (ΔH). There is also a correlation between ΔG and the reaction rate. The equilibrium constant (K) is defined as

$$K = e^{\frac{-\Delta G^o}{RT}}$$

where ΔG^o is the change in the standard Gibbs Free Energy, R is the ideal gas constant and T is the absolute temperature. It can also be shown that the equilibrium constant can be expressed as a ratio of forward and reverse reaction rates ($K = k_f/k_r$). This illustrates that more spontaneous reactions (more negative ΔG) have larger equilibrium constants (K) and will have a forward reaction rate constant that is larger than the reverse. Because (ΔG) depends only on the difference in the enthalpies (ΔH) for reactions of the form $B+CO_2 \rightleftharpoons BCO_2$, there is a direct positive correlation between enthalpy (ΔH) and rate constant.

This presents a key challenge for CO_2 capture technologies. From a practical perspective, it is desirable for rate constants for solvents and sorbents to exceed 12,000 per mole-per-liter per second (the green shaded region) and for reaction enthalpies to approximately fall between -40 kJ/mol and -75 kJ/mol (the blue shaded region). An ideal material for DAC, or PCC, would have parameters in the overlapping region, the white box in Figure 3B.1. No known systems have both parameters in this range because all existing CO_2 binding reactions are of the form $B+CO_2 \longrightarrow BCO_2$ and thus, the rate of the reactions increase as reactions become more exothermic. However, there is no fundamental reason that a CO_2 capture material must follow this trend. For example, it may be possible for a material to bind CO_2 via a reaction of the form $CO_2 + XYZ \longrightarrow X + Z + YCO_2$, so that DS > 0 for the reaction, and a fast, spontaneous reaction ($\Delta G << 0$) could have a lower binding energy, or even be endothermic. One way to achieve this may be to use a binding material that undergoes a phase change upon binding to CO_2. The enzyme carbonic anhydrase achieves similar results by creating a locally-high concentration of OH- and efficiently transferring the products and reactants.

While there are no known materials with the ideal characteristics described above, existing methods are currently being used to lessen the problem. For example, multiple amine types are often used in post-combustion capture research and development to form an absorbing solution with higher performance than any amine on its own. For example, a small amount of piperazine (~ 10% by volume) may be added to a MEA solution to increase the rate of CO_2 absorption [62].

Chapter 4: Conclusions

4.1 Limited roles for direct capture from air in climate change policy

Direct air capture (DAC), the subject of this report, involves the chemical sorption of dilute CO_2 *from flowing air and the release of concentrated* CO_2 *while regenerating these chemicals. Judgments about future roles for DAC and its future costs are necessarily constrained by the near absence of experimental results for DAC systems.* Today's state of knowledge is so limited that it is entirely possible that no DAC concept under discussion today will actually succeed in the field. Nonetheless, DAC has entered policy discussions and deserves close analysis. This report provides insights into how DAC relates to the mitigation of climate change now and in the future.

From the perspective of the next few decades, this report provides no support for arguments in favor of procrastination in dealing with climate change that are based on the imminent availability of DAC as a compensating strategy. Indeed, the limited experimental evidence available today strongly suggests that DAC will play at most a modest role in climate change mitigation over the next few decades. As a consequence, the pursuit of many currently promising mitigation options deserves higher priority. These options include end-use efficiency in all sectors of the economy, decarbonization of centralized energy sources, substitution of low-carbon electricity for gasoline and diesel fuel in vehicles, low-carbon fuels, forest protection, and strategies like afforestation and soil management that increase biological carbon storage on the land. However, one can invent scenarios where the relatively high cost of DAC would not be a deterrent. For example, the world could pay no effective attention to climate change for an initial period and then become worried. In seeking to move forcefully toward mitigation along many parallel tracks, the world might add DAC to the list of options, in view of its flexibility with regard to siting and scale and its relatively straightforward governance.

From a longer-term perspective, DAC could play a meaningful role in reducing the concentration of CO_2 *in the atmosphere. Nonetheless, given the large uncertainties in the future cost of DAC and other* CO_2 *removal strategies, century-scale economic models of global* CO_2 *emissions that feature "overshoot trajectories" should be viewed with extreme caution*, An overshoot trajectory is a trajectory of global CO_2 emissions that leads to a CO_2 concentration that climbs above its desired target and then falls back to the target from above. Overshoot trajectories sometimes emerge from economic models seeking cost-effective responses to climate change and assuming a future where 1) the risk of exceeding a stabilization target—even temporarily—is judged to be tolerable; 2) global economic growth has made every CO_2 mitigation option relatively less expensive; and 3) technological innovation has moderated the future costs of CO_2 removal. The latter part of an overshoot requires a sustained period of negative global CO_2 emissions, which can only be achieved by the vigorous deployment of deliberate CO_2 removal strategies. To contribute, DAC would need to be applied on a large scale, accompanied by a reliable system for long-term storage of CO_2 at that scale, and sustained over many decades.

DAC is not at all matched to the task of reacting quickly to a climate emergency. Its deployment is too slow. The required rates of construction of facilities above and below ground are out of reach. To find "fast" strategies that conceivably could be used to respond to a climate emergency, one must look elsewhere—possibly to a class of climate response strategies based on solar radiation management.

DAC is not the only way by which humanity might gradually compensate for its emissions or reduce the atmospheric CO$_2$ concentration. Among the alternatives are two terrestrial biological strategies: storage of additional carbon on the land and capture of CO$_2$ from bioenergy facilities. Storage of additional carbon on the land can be achieved by afforestation, reforestation, and the insertion of ecologically inert biomass (e.g., charcoal) into soil. Capture of part of the carbon in biomass can occur during the conversion of the biomass to power and fuels; it is a CO$_2$ reduction strategy as long as carbon sequestration from the atmosphere accompanies carbon capture, because the CO$_2$ that is captured was removed earlier from the atmosphere by photosynthesis. Biology-based capture strategies can bring environmental benefits beyond CO$_2$ removal from the atmosphere. Afforestation and reforestation, for example, can improve water storage and reduce erosion, and adding charcoal to soil may improve soil quality. However, biology-based strategies can either improve or worsen biodiversity and habitat for wildlife, and they will eventually come up against the constraint of limited land. DAC and biocapture strategies could co-exist.

The "net-carbon" issue for DAC excludes high-carbon energy sources. A capture system is ineffective if the CO$_2$ emissions associated with the energy to run the capture plant become comparable to the quantities of CO$_2$ that the plant removes from the input gas mixture. As a consequence, with today's available technology, DAC is incompatible with high-carbon energy sources (fossil fuels burned without accompanying CO$_2$ capture and storage), and even capture of CO$_2$ from power plants sources is hobbled. One way around the net-carbon problem for DAC is to generate power and heat from fossil fuels at the DAC site and to capture the CO$_2$ from these facilities. Subsequent steps would involve a unified system to transport and store the CO$_2$ captured from both the local energy production plants and the DAC facility. Other approaches would use non-carbon (renewable or nuclear) energy sources.

Low-carbon "leakage" constrains even decarbonized energy sources. Even when all the energy required for air capture is provided by dedicated and fully decarbonized energy sources (a local nuclear power plant or a local solar-thermal power plant with associated hydropower storage, for example), it is still appropriate to assign CO$_2$ emissions to the energy source, if the larger regional energy system is not fully decarbonized. In a world where high-carbon centralized CO$_2$ sources are still in existence, any low-carbon energy system deployed to drive DAC could have displaced such a centralized source instead. When this is the case, the carbon intensity of the entire regional system would be a better measure to use in determining the net CO$_2$ emissions of the DAC system. This form of geographical "leakage" of low-carbon energy systems into DAC would get attention in careful global carbon accounting.

4.2 Cost-dependent roles for DAC

There are three distinct areas where the cost of CO$_2$ capture from air will strongly affect its future role: a) centralized uses of fossil fuels, b) distributed uses of fossil fuels, and c) atmospheric CO$_2$ removal. Based on the detailed analysis of one DAC option that could be built today and an exploration of the underlying science that may permit cost reductions over time, this report concludes that: a) DAC makes sense only after the world has captured nearly all of the CO$_2$ from whatever centralized fossil-fuel facilities are operating; b) DAC could have some role in compensating for distributed emissions, specifically those that are not well matched to electrification or low-carbon fuels, and c) the principal role of DAC may be to reduce the atmospheric CO$_2$ concentration, jointly with other CO$_2$ removal strategies.

To get a rough sense of relative costs, this report uses a common methodology and many common cost assumptions to compare the costs of a benchmark DAC system and a reference post-combustion-capture (PCC) system that could be retrofitted to a coal power plant to capture CO$_2$ from flue gas. The costs in both cases are for systems that could be built today. The reference avoided cost for CO$_2$ capture from flue gas is estimated to be about \$80/tCO$_2$. The estimated avoided cost of the benchmark DAC system is in the range of \$600 per metric ton of CO$_2$, and significant uncertainties in the process parameters result in a wide, asymmetric range associated with this estimate, with higher values being more likely than lower ones. Future cost reductions in PCC and DAC systems arising from technological innovation and learning by doing are not estimated.

Note that although the concentration of CO$_2$ in air is 300 times less than in coal-based flue gas, our estimate of the ratio of avoided costs is eight, far below 300. Concentration issues do not drive the design of flue-gas capture to anything like the extent that they would drive DAC. As a result, an air-capture facility would not resemble a flue-gas-capture facility three hundred times larger.

Coherent CO$_2$ mitigation would appear to require only limited deployment of DAC until CO$_2$ is captured from nearly all large centralized facilities. Based on currently available information about likely costs, DAC can be expected to be more expensive than capturing at least 90% of the CO$_2$ present in the concentrated effluent streams from such facilities—which include coal and natural gas power plants, cement plants, steel plants, and chemical plants. The

underlying reason for the limited competitiveness of DAC is that CO_2 is such a dilute constituent of air. Only one molecule in 2500 in air today is CO_2, and the concentration of CO_2 in air is about 300 times less than in the flue gas from a coal power plant. The low concentration inevitably requires the movement of large quantities of air, with associated costs. DAC does have some cost advantages relative to PCC, as a result of a lower intake temperature, fewer feed contaminants, and flexibility in siting that could allow use of lower-cost, "stranded" energy resources. However, these advantages are unlikely to outweigh the severe concentration penalty.

DAC could compensate for some emissions from decentralized energy sources. In compensating for recalcitrant decentralized CO_2 emissions, the extent to which DAC would be the CO_2-removal strategy of choice will depend on how well it competes with other options. In addition to improvements in energy efficiency, there are two important alternative paths to decarbonization of decentralized emissions, such as emissions from buildings and vehicles: 1) electrification of the use, accompanied by decarbonization of electricity, 2) substitution of low-carbon fuel, biologically derived or produced in some other way. Both of these paths face uncertainties: the future performance of batteries and fuel cells is unclear, as are the upper limits on the availability of low-carbon fuel. When the cost of some mitigation or adaptation measure exceeds the cost of CO_2 removal from the atmosphere, it will be more cost-effective to remove the carbon from the atmosphere after it has been emitted than to prevent its emission in the first place. Some future mitigation and adaptation options that today appear to be very costly may never be needed.

System design will be strongly affected by local environmental operating conditions. Average values—as well as seasonal and short-term variability—of temperature, humidity, wind, and pollution content of outdoor air will strongly affect the choice of sorbents and sorption-desorption strategies.

The land requirements for a DAC facility are small, relative to its biological competitors However, the DAC footprint includes not only the structures through which the air flows over reactive chemicals, but also the facilities providing electricity, thermal energy, and water and the pipelines and injection wells connecting the capture site with storage sites in deep geological formations.

The storage part of CO_2 *capture and storage (CCS) must be inexpensive and feasible at huge scale for DAC to be economically viable.* The commercialization of CCS requires the resolution of formidable reservoir-engineering challenges to achieve efficient injection of CO_2 in geological formations for multi-hundred-year storage. Alternatives to geological storage are also under consideration, notably mineral carbonation, where CO_2 is fixed as carbonate through reaction with natural silicates (very abundant on earth) or alkaline industrial residues.

In principle, any concentrated stream of CO_2 *produced by DAC or industrial* CO_2 *capture could be recycled into "low-carbon" fuels, such as "low-carbon diesel."* CO_2 recycle into fuels is sometimes proposed as an alternative to CO_2 disposal. To be sure, such a strategy presumes success in DAC development. CO_2 recycle is a conceivable strategy for a world that is determined to be both carbon-neutral and hydrocarbon-powered and that is confronting limits on biofuels.

DAC could be at a disadvantage in competitions for CO_2 *management.* Both CO_2 captured from air (whether chemically or biologically) and CO_2 captured from power plants and other industrial facilities could enter the same end-of-pipe systems (pipelines and wells, for example). DAC, at best, will be a late arrival and might well find that the best storage sites are already spoken for. However, the siting flexibility of DAC could allow access to additional destinations.

4.3 Pedagogy

This report has targeted a broad audience of scientists and engineers in order to encourage expansion of the limited technical discussion that has occurred to date and to encourage entrants into the field. The intention throughout has been to demystify, to explain unfamiliar vocabulary, to work through representative calculations. Making the subject of a technology assessment more available to the non-specialist is an objective that other assessments could pursue.

Symbols and other Notation

A: frontal area

BCO_2: CO_2-bound complex

C_{avo} : cost per ton of CO_2 avoided

C_{cap}: cost of CO_2 captured

C_o: CO_2 concentration in air

c_Q: carbon intensity of external heat input

c_W: carbon intensity of work input

D : diffusivity

d : diameter

E: Energy per unit time required to move air [J/s]

e : emphasizes that the separation energy is provided by electricity

ΔG : Gibbs Free Energy change

ΔH : enthalpy

K : equilibrium constant

k_f: rate constant for a forward reaction

k_r: rate constant for a reverse reactions

L :length

M : molarity

$M-CO_2$: Capture rate [kg/s]

M_{avo}: "avoided" emissions

M_{cap}: gross amount of CO_2 captured

M_{CO2} : molar mass of CO_2 (44 g/mol)

M_{H2O} : molar mass of water (18 g/mol)

n : moles of a gas mixture at atmospheric pressure

n_{cap} : number of moles of captured CO_2

n_{em} : total number of moles of the remaining gas that are emitted

Pa : Pascal

P_{drop} : pressure drop

P_{eq} : equilibrium partial pressure of water

$P_v(T)$: temperature:dependent vapor pressure

P_w: partial pressure of water vapor

P_e : Peclet number

Q : external heat input (Chapter 2), volumetric flow rate of air through contactor (Appendix 3A)

R : ideal gas constant (8.314 J/mole:K)

R_H : relative humidity

R_e : Reynolds number

ΔS : entropy

S_c : Schmidt number

S : degree of saturation

s : entropy per unit mole of any gas mixture

s_{em} : molar entropy of a final mixture that contains CO_2 that is not captured

U : velocity

W : work input

w_{min} : unit mass of CO_2 captured

x : mole fraction of one component

x_w : water mole fraction

y : CO_2 mole fraction

z : CO_2 mole fraction in the emitted gas

α : fraction of CO_2

η : dimensionless parameter related to the fraction of CO_2 captured

v : dynamic viscosity of air (1.8×10^{-5} Pa-s)

ρ : gas density

Physical units

BTU : British thermal unit

GJ : gigajoule, one billion Joules

Gt : gigaton, one billion tons

kJ : kilojoule, one thousand Joules.

MJ : megajoule, one million Joules

MW : megawatt

MWh : megawatt hours

ppm : parts per million

tCO_2 : tons carbon dioxide

Chemical formulas

CaCO$_3$: calcium carbonate, limestone

CH$_4$: methane

CFC-12 : (CCl$_2$F$_2$)

CFC-11 : (CCl$_3$F)

CO$_3$$^{2-}$: carbonate ion

HCO$_3$: bicarbonate ion

H$_2$CO$_3$: carbonic acid

Na$_2$CO$_3$: sodium carbonate, soda ash

NaOH : sodium hydroxide, lye

N$_2$O : nitrous oxide

NO$_x$: nitrogen oxides (NO, NO$_2$)

SO$_x$: sulfur oxides (SO$_2$, SO$_3$)

Acronyms

BECS : Biological Energy with Carbon Storage

CCS : Carbon Capture and Storage

CDR : Carbon Dioxide Removal

DAC : Direct Air Capture

FGD : Flue Gas Desulfurization

ISBL : Inside Battery Limits

MEA : Monoethanolamine

MOFs : Metal-Organic Frameworks

NETL : National Energy Technology Laboratory

NGCC : Natural Gas Combined Cycle

OSBL : Outside Battery Limits

PCC : Post:Combustion Capture

RTSA : Rapid Temperature-Swing Adsorption

SRM : Solar Radiation Management

Glossary

absorbent: A bulk solution that reacts with a molecule so that the molecule is either chemically or physically bound to the solvent.

absorber: see **contactor**

absorption: The chemical or physical incorporation of molecules into a bulk solution.

acid: A molecule that accepts electron density (Lewis theory) from or donates a proton, H+ (Bronsted theory), to another molecule, a base.

activation energy: The energy barrier that must be overcome in order for a chemical reaction to occur.

adsorbent: A solid material that either physically or chemically binds a molecule to its surface.

adsorption: The chemical or physical binding of a molecule onto the surface of an adsorbent.

afforestation: A biologically based geoengineering method in which the stock of biomass in forest is increased.

amine: An basic organic molecule with the general form NR_3 where R = organic functional group or a hydrogen atom, and the nitrogen atom is the basic site.

amphoteric: A descriptor of a molecule that acts as both an acid and a base.

anion: A negatively charged ion.

anthropogenic source: A man made source.

air separation unit: A facility that produces industrial gases (N_2, O_2 or Ar) from air.

avoided CO_2 emissions (M_{avo}): The amount of CO_2 is avoided in a capture process after subtracting out the CO_2 emissions from the heat and power used to run the process.   This is expressed mathematically in Box 2.4. Alternatively, when considering power plants, the amount of CO_2 emissions from a similarly fueled power plant without carbon capture that exports the same amount of electricity as the power plant with carbon capture.

base: A molecule that donates electron density (Lewis theory) to, or accepts protons, H^+ (Bronsted theory) from, another molecule, an acid.

battery limit: The boundary of a process plant. Capital costs within battery limit are referred to as the inside battery limit (ISBL) costs. Everything else, such as waste treatment or heat and power utilities, is an outside battery limit (OSBL) cost.

bicarbonate ion (HCO_3-): The conjugate base of carbonic acid. Some bicarbonate is formed when carbon dioxide is dissolved in water.

binding energy: A measure of the strength of the bond between two reactants in a binding reaction of the form A + B à AB.

biomass: Biological material from living or recently living organisms.

biopower with CCS: A biologically based method of geoengineering in which crops from a dedicated plantation are used as fuel at a power plant and to capture and sequester the resulting CO_2 from the plant. Also called BECS–Biological Energy with Carbon Storage.

buffer: A mixture of a weak acid and its conjugate base or a weak base and its conjugate acid that maintains the pH of a solution in a narrow range when acids or bases are added.

$CaCO_3$: see **calcium carbonate**

calciner : A thermal treatment facility that is applied to solid materials to cause decomposition, phase transition or the removal of a fraction of the mixture. The name is derived from the decomposition of limestone ($CaCO_3$) into lime (CaO) and CO_2 in the cement industry.

calcium carbonate ($CaCO_3$): A calcium salt of carbonic acid which has low solubility in water.

calcium hydroxide ($Ca(OH)_2$): A strong basic chemical, also called slaked lime.

capital cost: The initial setup costs for a system which enable it to operate, after which there are only recurring operating costs.

$Ca(OH)_2$: see calcium hydroxide.

carbonate ion (CO_3^{2-}): The conjugate base of the bicarbonate ion (HCO_3^-)

carbonic acid (H_2CO_3): The product of the hydration of carbon dioxide in water solution: $CO_2 + H_2O \longrightarrow H_2CO_3$.

carbonic anhydrase: Metalloenzyme that catalyzes the conversion from carbon dioxide to carbonic acid and to bicarbonate with a loss of a proton.

carbamate ($RNHCOO^-$): The conjugate base of carbamic acid. The carbamate ion is formed when CO_2 reacts an amine: $CO_2 + 2RNH_2 \longrightarrow RNHCOO^- + RNH_3^+$.

carbon dioxide removal (CDR): A method of geoengineering in which carbon dioxide is removed from the atmosphere. This term includes direct air CO_2 capture, enhanced oceanic uptake, biopower with CCS and others.

catalyst: A molecule that lowers the activation energy of a reaction without being consumed during the reaction.

cation: A positively charged ion.

CCS: Carbon dioxide capture and storage.

CO_2 sequestration: A process in which high pressure CO_2, often in a supercritical state, is injected underground into geological formations. There are other forms of CO_2 sequestration, such as ocean and mineral storage, but in this report, definitions are limited to geological CO_2 storage.

concentrated emissions: Emissions from a large stationary CO_2 source, such as a power station.

contactor: The portion of an industrial gas separation system in which the gas of interest is absorbed or adsorbed.

cyclic process: A thermodynamic process which begins from and finishes at the same thermostatic state

decarbonize: To remove carbon by chemical means.

deforestation: Clearing forests for human activity.

desorb: To change from an adsorbed or absorbed state on a surface or within a liquid to a gaseous state.

desorber: See regenerator

diffuse emissions: Emissions from distributed sources, such as transportation.

direct capture from air (DAC): a process to capture CO_2 directly from ambient air

drift: see **misting**

endothermic: A descriptor for a chemical reaction that consumes heat or requires heat to drive it.

enthalpy (ΔH): A thermodynamic quantity equal to the internal energy of a system plus the product of its volume and pressure. Here, the change in enthalpy for a reaction (ΔH) refers to the binding energy of the reaction.

entropy: The measure of disorder in a system. A thermodynamic quantity that changes in a reversible process by an amount equal to the heat absorbed or emitted divided by the thermodynamic temperature.

enzyme: Proteins that accelerate the rates of chemical reactions (act as catalysts) in biological systems without being consumed during the reaction.

equilibrium constant (K_{eq}): A dimensionless quantity that describes a chemical equilibrium. It is defined as $K_{eq} = exp(-\Delta G_0/RT)$ where ΔG_0 is the standard Gibbs free energy change between the reactants and products of a reaction at the operating temperature, R is the ideal gas constant and T is the temperature. The ratio of the concentrations of the products and reactants in a reaction (to the power of the corresponding stoichiometric coefficient in the reaction) must be equal to Keq at equilibrium. $K_{eq} > 1$ indicates that the products, i.e. the forward reaction, are favored and $K_{eq} < 1$ indicates that the reactants, i.e. the backward reaction, are favored.

exothermic: A descriptor for a chemical reaction that evolves heat.

flue gas: Gases that are produced from the combustion of fuel.

flue gas desulphurization (FGD): A process in which SO_2 is removed from flue gas exhausts from power plants.

geoengineering: The deliberate planetary manipulation that is proposed as a strategy to reverse the effects of global warming.

Gibbs free energy (G): Gibbs free energy reaches a minimum when equilibrium is achieved at a given temperature and pressure. The direction of decreasing G tells us which way a system will evolve as it tries to reach equilibrium. It is defined as $G = E + PV - TS$, where E is the internal energy, P is the pressure, V is the volume, T is the temperature and S is the entropy. The Gibbs free energy of a reaction (ΔG) is the difference between the Gibbs free energy of the reactants and that of the products.

hectare (ha): 10,000 square meters

Henry's law: A law stating that at a constant temperature the amount of gas that will dissolve into a solution is proportional to the partial pressure of the gas above the solution. In mathematical terms, $p = k_H C$ where p = partial pressure of the gas, k_H = Henry's law constant and C = the solute concentration.

hydroxide: A basic diatomic anion, OH^-.

ionic liquids: Salt compounds that are liquid at room temperature and pressure.

ISBL factor: The total capital cost for a process can be estimated at early stages of its development by multiplying the major equipment purchase cost by an ISBL factor. The ISBL factor generally varies from 2 to 6 depending on the process.

IGCC: Integrated gasification combined cycle, or a power plant in which coal is converted to synthesis gas (syngas, a mixture of hydrogen and carbon monoxide) that is used to drive gas combustion and steam turbines after conversion of carbon monoxide into carbon dioxide and its removal from hydrogen. In some cases CO_2 formed in the synthesis gas may be captured prior to feeding the gas turbine.

ion exchange resin: Polymers that exchange ions in the polymer with ions in a solution.

ion strength: The concentration of ions (cations or anions) in a solution.

laminar flow: A flow condition in which fluid flows in layers with no disruption between the layers; the opposite of turbulent flow.

lime: CaO

mass transfer: The transfer of molecules from regions of high concentration to regions of low concentration.

MEA: monoethanolamine [$NH_2(CH_2CH_2OH)$]

metal: a chemical element that is a conductor of electricity and readily loses electrons to form cations.

metal oxide: A chemical compound containing metal and oxygen atoms.

misting: The physical loss of a solvent during liquid phase transport. See **drift**.

mole fraction: the ratio of the number of moles of one constituent of a mixture or solution to the total number of moles of all the constituents.

Na_2CO_3: see **sodium carbonate**

NaOH: see **sodium hydroxide**

natural gas scrubbing: The process by which gas is purified to rid of contaminants (e.g., sulfur compounds, carbon dioxide).

negative emissions: A decrease in the atmospheric CO_2 concentration.

NO_x: Nitrogen oxide compounds, including NO, NO_2 and N_2O.

NGCC: Natural gas combined cycle, or a natural-gas fired power plant with both gas and steam turbines.

operating cost: The recurring cost associated with regular operations of a system.

packing material: Materials used to increase contact between two phases, such as in absorption or separation processes. Packing material can be random or structured and made of materials such as ceramic, plastic or metal.

partial pressure: Pressure from one component in a gas mixture.

pH: A measure of the concentration of protons (acidity) of a solution. It is expressed mathematically as the negative logarithm of the hydrogen ion concentration.

piperazine ($C_4H_{10}N_2$): A basic organic compound used to increase the rate of CO_2 absorption in post-combustion capture.

post-combustion capture (PCC): A process that captures CO_2 from power plant flue gases; flue gas is cooled and fed into the bottom section of a CO_2 absorber where it passes through an absorbing solution, containing a chemical to capture the CO_2.

precipitator: process equipment used to isolate a solid material from the species in solution and the solvent; this can be accomplished by cooling the solution, by reacting the target compound with a proper chemical (to form an insoluble salt for instance) and/or by evaporating the solvent.

pressure drop: The loss of pressure as a gas flows through an absorber unit.

rate constant: A constant that quantifies the speed of a chemical reaction. The rate constant depends on the conditions of the reaction.

regenerate: To restore or be restored to an original physical or chemical state.

regenerator: The portion of a gas separation systems in which the bound molecule, CO_2, is released from the ab/adsorbing material into the gas phase.

Reynolds number: A dimensionless constant in fluid mechanics that is a ratio of inertial and viscous forces. A low Reynold's number corresponds to smooth flow (laminar flow) and a high Reynold's number corresponds to turbulent flow.

slake: A common treatment for lime in which it crumbles when exposed to water.

silica: Silicon dioxide (SiO_2).

sodium carbonate (Na$_2$CO$_3$): A sodium salt of carbonic acid, also called soda ash, and is a strong base.

sodium hydroxide (NaOH): A strong basic chemical, also called lime or caustic soda.

solar radiation management (SRM): A type of geoengineering in which the amount of solar radiation that is reflected back into space from the surface of the earth is increased.

solvent: A liquid substance, in which another material is dissolved.

sorbent: A material used for either absorption or adsorption.

SO$_x$: Sulfur oxide compounds, including sulfur dioxide, SO$_2$, and sulfur trioxide, SO$_3$.

spray tower: Equipment used in pollution control technology. Typically, nozzles are used to spray an absorbing liquid from the top of the tower and a gas mixture flows into the tower from the bottom.

stripper column: A portion of a gas separation system in which the gas is removed from the binding material.

surface tension: A property of liquids caused by unequal molecular forces near the surface that causes the surface area of a liquid to be minimized.

zwitterion: A molecule that contains both a positively charged center (cation) and negatively charged center (anion) within the same molecule.

Biographies of the Study Committee Members

ROBERT H. SOCOLOW (*Study Co-Chair*)

Robert Socolow is a Professor of Mechanical and Aerospace Engineering at Princeton University. He is the Chair of the Panel on Public Affairs of the American Physical Society. Socolow earned a Ph.D. in theoretical high energy physics in l964 from Harvard University. He was an assistant professor of physics at Yale University from l966 to l97l. He is a Fellow of the American Physical Society and the American Association for the Advancement of Science. He received the 2009 Frank Kreith Energy Award of American Society of Mechanical Engineers; the 2005 Axelson Johnson Commemorative Lecture award of the Royal Academy of Engineering Sciences, Sweden; and the 2003 Leo Szilard Lectureship Award, American Physical Society. He was a Member, Grand Challenges for Engineering Committee of the U.S. National Academy of Engineering. Socolow's current research focuses on the characteristics of a global energy system responsive to global and local environmental and security constraints. He was a member of the Committee on America's Energy Future and is a current member of the Committee on America's Climate Choices, both at the National Academy of Sciences. He is the co-principal investigator (with ecologist, Stephen Pacala) of Princeton University's Carbon Mitigation Initiative (CMI) www.princeton.edu/~cmi/, a fifteen-year (2001-2015) project, supported by BP and Ford. Socolow was the editor of *Annual Review of Energy and the Environment*, 1992-2002. With John Harte, Socolow co-edited *Patient Earth* (Holt, Rinehart, l97l), one of the first college textbooks in environmental studies.

MICHAEL J. DESMOND (*Study Co-Chair*)

Mike Desmond is a distinguished advisor within BP Refining and Marketing's Research and Technology department, and is involved with helping develop BP's technology program for converting unconventional feedstocks to fuels. His research activities at BP in homogeneous and heterogeneous catalysis, zeolite synthesis, and energy storage led to over 20 patents and a number of publications/presentations. During a 30 year career with BP, Mike has held a number of technology and commercial management roles, including manager of UK supply planning and US wholesale marketing for BP Refining and Marketing as well as director of business development and vice president of technology for BP Chemicals Inc. Mike has a B.S. in Chemistry from the University of Notre Dame, a Ph.D. in Inorganic Chemistry from the University of Illinois and an MBA from John Carroll University.

ROGER AINES

Dr. Roger Aines is the Carbon Fuel Cycle Program Leader, and a Senior Scientist in the Physical and Life Sciences Directorate at Lawrence Livermore National Laboratory (LLNL). He holds a Bachelor of Arts degree in Chemistry from Carleton College, and Doctor of Philosophy in geochemistry from the California Institute of Technology. He has been at LLNL since 1984 working on nuclear waste disposal, environmental remediation, application of stochastic methods to inversion and data fusion, management of carbon emissions including separation technology, and monitoring and verification methods for sequestration. Roger's career has involved a close coupling of scientific research, engineering, field demonstration, and assessment of future development needs for technology with an emphasis on the transition of scientific projects from benchtop to pilot and field scale. His research interests include the chemistry of natural and engineered processes, including carbon dioxide separation and water treatment. The Carbon Fuel Cycle Program takes an integrated view of the energy, climate, and environmental aspects of carbon-based fuel production and use. It supports DOE projects in sequestration technology development for capture, and underground coal gasification. It provides key support to major international sequestration projects at In Salah, Weyburn, and the US Partnerships. Roger led LLNL's development of stochastic inversion and data fusion techniques known as the stochastic engine. This is currently being applied to monitor oil field injection and is being developed to monitor CO$_2$ sequestration. Roger holds eight patents in the area of in situ degradation of organic chemicals through heating, simulation of steam-driven underground processes in heterogeneous media, and the mechanisms of thermally assisted remediation.

JASON J. BLACKSTOCK

Jason Blackstock is a Research Scholar at the International Institute for Applied Systems Analysis, where his research focuses on evaluating the scientific (climatic) and socio-political implications of geoengineering (or climate engineering) schemes. His research includes both a rigorous examination of the science underlying the full range of geoengineering schemes, and an assessment of the *international* political and social consequences of considering— and potentially testing and/or implementing—such schemes. Important components of both the physical and social science evaluations are quantitative risk and uncertainty assessments, leading toward the development of decision frameworks for addressing high-risk, high-uncertainty alternatives. Blackstock received his Ph.D. in Physics (2005) from the University of Alberta in Canada, his Graduate Certificate in International Security (2006) from Stanford, and his Master of Public Administration (2008) from Harvard's Kennedy School. He is also currently a Fellow of the Center for International Governance Innovation in Waterloo Canada, and has previously served as a Researcher (Belfer Center for Science and International Affairs) and Teaching Fellow (Faculty of Arts and Science) at Harvard University, a Research Associate in Hewlett Packard's Quantum Science Research Group, and a Senior Fellow at the University of Toronto in the Trudeau Centre for Peace and Conflict Studies.

OLAV BOLLAND

Olav Bolland is Professor of Thermal Power Engineering in the Department of Energy and Process Engineering at the Norwegian University of Science and Technology (NTNU). His research includes a large range of power plant modelling and simulations, including that of CO_2 capture methods (pre-, post-, and oxy-combustion). The methodologies are both theoretical and experimental. The theoretical work includes cycle design with several state-of-the-art software tools, transient modelling and simulation, methodology related to generalisation of efficiency penalty in CO_2 capture, and exergy analysis for pre- and post-combustion CO_2 capture methods. The experimental work is within so-called "Chemical Looping Combustion," where the oxidation and reduction of metals is studied in two experimental set-ups. He has been active in this area since 1989. Other fields of interest and research include solid oxide fuel cells— modelling and simulation, and particle technology. He was Lead Author for the IPCC's Special report on CO_2 Capture and Storage, which was published in 2005. As one of the IPCC scientists researching climate change, he received the 2007 Nobel Peace Prize. Since 2005, he has been a Member of the Advisory Board for the international research project CCP2 and CCP3 (Carbon Capture Project) and he has been Associate Editor for the Journal of Greenhouse Gas Control since 2006. Also since 2006 he has been an elected member of The Norwegian Academy of Technical Sciences (NTVA). In 2008-2009 Bolland was the director of the Gas Technology Centre NTNU-SINTEF, and since 2009 he has been the head of the Department of Energy and Process Engineering at NTNU.

TINA KAARSBERG

Tina Kaarsberg serves as the co-chair of the American Physical Society's Panel on Public Affairs' Energy and Environment subcommittee and as a Team Leader of the Geothermal Technologies Program at the U.S. Department of Energy. She received her B.A. (with Distinction in Physics) from Yale University in 1982. She conducted her thesis research in experimental particle physics as a Fellow at Cornell University. She received a Ph.D. in Physics from Stony Brook University in 1988. Kaarsberg then accepted a UCLA Physics Department research faculty position, and conducted research at Brookhaven National Laboratory. In 1991, she was selected as an APS Congressional Science Fellow and after a break to have the first of her two children, went to work for Senator Pete V. Domenici. From 1993 to 1999, Dr. Kaarsberg worked-as a contractor and grantee-for the Department of Energy with Sandia National Laboratories, and the Northeast-Midwest Institute. In 1999, Dr. Kaarsberg was recruited to lead the Power Technologies Analysis Collaborative for the DOE's Office of Energy Efficiency and Renewable Energy. From 2002-2005, Dr. Kaarsberg worked as a Professional Staff member for the House of Representatives' Committee on Science with responsibilities for distributed energy, energy efficiency, renewable, climate change technology, and basic science programs at DOE. In 2005, she returned to DOE as a Senior Policy Analyst for the Assistant Secretary for Policy and International Affairs. In this position, she led policy reviews of budget proposals for DOE's Office of Science, Energy Efficiency and Renewable Energy, Electricity, and Nuclear Energy. She also has advised on energy efficiency, renewable energy, and climate technology policy initiatives. Dr. Kaarsberg co-authored several dozen physics papers and has published more than 50 policy related papers. She has received numerous honors and awards including an 'Unsung Hero' Award from the Climate Institute. Dr. Kaarsberg has served in many positions within the APS Forum on Physics in Society including her election as Vice-Chairman in 2003. She also has served in several elected capacities for the American Association for the Advancement of Science and is a Fellow of the APS.

NATHAN LEWIS

Dr. Nathan Lewis, George L. Argyros Professor of Chemistry, has been on the faculty at the California Institute of Technology since 1988 and has served as Professor since 1991. He has also served as the Principal Investigator of the Beckman Institute Molecular Materials Resource Center at Caltech since 1992. From 1981 to 1986, he was on the faculty at Stanford, as an assistant professor from 1981 to 1985 and as a tenured Associate Professor from 1986 to 1988. Dr. Lewis received his Ph.D. in Chemistry from the Massachusetts Institute of Technology. Dr. Lewis has been an Alfred P. Sloan Fellow, a Camille and Henry Dreyfus Teacher-Scholar, and a Presidential Young Investigator. He received the Fresenius Award in 1990, the ACS Award in Pure Chemistry in 1991, the Orton Memorial Lecture award in 2003, the Princeton Environmental Award in 2003 and the Michael Faraday Medal of the Royal Society of Electrochemistry in 2008. He is currently the Editor-in-Chief of the Royal Society of Chemistry journal, Energy & Environmental Science. He has published over 300 papers and has supervised approximately 60 graduate students and postdoctoral associates. His research interests include artificial photosynthesis and electronic noses. Technical details of these research topics focus on light-induced electron transfer reactions, both at surfaces and in transition metal complexes, surface chemistry and photochemistry of semiconductor/liquid interfaces, novel uses of conducting organic polymers and polymer/conductor composites, and development of sensor arrays that use pattern recognition algorithms to identify odorants, mimicking the mammalian olfaction process.

MARCO MAZZOTTI

Marco Mazzotti, an Italian citizen born in 1960, married, with two children, has been professor of process engineering at ETH Zurich since May 1997 (associate until March 2001 and full professor thereafter). He holds a Laurea (M.S., 1984) and a Ph.D. (1993), both in Chemical Engineering and from the Politecnico di Milano, Italy. Before joining ETH Zurich, he had worked for IBM Italy (1985-1987) and Montefluos (1988-1990), and had been assistant professor at the Politecnico di Milano (1994-1997). His research activity deals with adsorption-based separations and chromatography, and with crystallization and precipitation processes. The application areas of interest are the purification of biopharmaceuticals and the development of carbon dioxide capture and storage systems. He teaches classes on Separation Processes, Mathematical Methods for Chemical Engineers, Phase Equilibria and Carbon Dioxide Capture and Storage. Twenty-two Ph.D. students have graduated with him and thirteen are currently advised by him. His refereed publications include more than 180 journal articles, 20 articles in books and 6 book chapters. He has been coordinating lead author of the IPCC Special Report on Carbon Dioxide Capture and Storage (2002-2005). He is also an active member of the AIChE, of the Working Party on Crystallization of the EFCE, and he is President of the International Adsorption Society. He was the chair of the 9th International Conference on Fundamentals of Adsorption FOA9 (Italy, May 20-25, 2007), and will be the chair of the 18th International Symposium on Industrial Crystallization (Switzerland, September 13-16, 2011).

ALLEN PFEFFER

Allen Pfeffer serves as Senior Expert for the Boiler/Environmental Segment at ALSTOM Power, a global leader in equipment and services for power generation and rail transport. He earned a Ph.D. in Mathematics from the California Institute of Technology in 1966 and has over 30 years of experience in gas turbine, boilers, and steam turbine research, design, and program management. He has significant experience in developing and directing a Total Quality Management Process and in forming work teams to analyze and solve critical problems in R&D and total power plant integration. Previous to his current position, he served as Managing Director of Technology at ALSTOM Power from Aug. 2000—March 2004 for the Power, Gas Turbine Segment and previous to this was Director of Research & Development at ALSTOM Power for the Boiler Segment Worldwide. He served as Vice President - ABB Product Development and Technology, Windsor, CT, and Vice President - Program Manager for Combustion and Fluid Dynamics, ABB Baden, Switzerland, directing the ABB worldwide Corporate Programs in Combustion and CFD technology, concentrating on identifying new technical products for Industrial Gas turbines, Steam turbines and Boilers. He is a primary author of "Options for Gas Turbine Power Generation with Reduced CO$_2$ Emissions," which is an overview of ongoing activities to study and develop options for carbon dioxide (CO$_2$) emissions reductions from gas turbine power generation and a co-author of The Potential of Clean Conventional Coal vs. IGCC, GT2006—90890, a vision for clean coal power.

JEFFREY J. SIIROLA

Jeff Siirola is currently a Technology Fellow in the Eastman Research Division of Eastman Chemical Company in Kingsport, Tennessee, where he has been for 38 years. He received a B.S. in chemical engineering from University of Utah in 1967 and a Ph.D. in chemical engineering from the University of Wisconsin-Madison in 1970. His areas of interest include chemical process synthesis, computer-aided conceptual process engineering, engineering design theory and methodology, chemical process development and technology assessment, resource conservation and recovery, sustainable development and growth, artificial intelligence, non-numeric computer programming, and chemical engineering education. Siirola serves on the Board of Directors of ABET (formerly, Accreditation Board for Engineering and Technology). He is also a trustee and past president of CACHE (Computer Aids for Chemical Engineering Education), and a member of the American Chemical Society, the American Association for Artificial Intelligence, and the American Society for Engineering Education. He has served on numerous National Science Foundation and National Research Council panels, and on the advisory boards of several journals and chemical engineering departments. Siirola is a member of the National Academy of Engineering and was the 2005 President of the American Institute of Chemical Engineers.

KARMA SAWYER

Karma Sawyer is an ARPA-E and AAAS Science and Technology Policy Fellow at the Department of Energy in the Advanced Research Projects Agency—Energy (ARPA-E). Her work focuses on transformative materials and processes for carbon capture and sequestration as well as novel catalysts and processing for creating synthetic liquid fuels from natural gas. Sawyer received a B.S. with Honors in Chemistry from Syracuse University in 2003 and was named a Syracuse University Scholar (2003) and a Goldwater Scholar (2002). She received a Ph.D. in Chemistry from the University of California at Berkeley in 2008. In graduate school, she studied spin-crossover dynamics and homogeneous catalysis reactions using ultrafast infrared spectroscopy and density functional theory (DFT) calculations. As a postdoctoral scholar in the Department of Mechanical Engineering in the University of California at Berkeley, she investigated phonon localization in silicon nanowires for thermoelectric applications and photoinitiated methods of carbon capture.

BEREND SMIT

Berend Smit received his MSc in Chemical Engineering and MSc in Physics from the Technical University in Delft (the Netherlands) in 1987, followed by his PhD in Chemistry from Utrecht University (the Netherlands) in 1990. In 2004, Smit was elected Director of the European Center of Atomic and Molecular Computations (CECAM) Lyon France, and since 2007, he has been Professor of Chemical Engineering and Chemistry at the University of California in Berkeley. Smit has published over 200 scientific papers and received the Gold Medal of the Royal Dutch Chemical Society for his research. His current research involves the development and application of molecular simulation techniques. Previously, Smit was a (senior) Research Physicists at Shell Research (1988-1997) and Professor of Computational Chemistry at the University of Amsterdam (1997-2007).

JENNIFER WILCOX

Jennifer Wilcox has been an Assistant Professor in the Department of Energy Resources Engineering at Stanford University since 2008. Her Ph.D. in Chemical Engineering in 2004 is from the University of Arizona, and her B.A. in Mathematics in 1998 is from Wellesley College. She received the 2007 ARO Young Investigator Award (Membrane Design for Optimal Hydrogen Separation), the 2006 ACS PRF Young Investigator Award (Heterogeneous Kinetics of Mercury in Combustion Flue Gas), and the 2005 NSF CAREER Award (Arsenic and Selenium Speciation in Combustion Flue Gas). Within her research group, high-level ab initio methods (i.e., CCSD(T)) are used to calculate gas-phase kinetics for trace metal (Hg, As, Se) oxidation reactions. A custom-built electron ionization quadrupole mass spectrometer is used for the direct measurement of trace metals to benchmark gas-phase kinetic predictions and to test sorbent/catalytic potential of well-characterized materials. Plane-wave-based density functional theory methods are used to probe and understand molecular-level gas-surface interactions using density of states analyses. Her research involves the coupling of theory to experiment to test newly-designed materials for sorbent or catalytic potential.

Internal Reviewers

Renato Baciocchi, Universita' di Roma

Peter Eisenberger, Columbia University

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David Hawkins, National Resources Defense Council

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Edward Parson, University of Michigan

George Richards, U.S. Department of Energy

Doug Ruthven, University of Maine

Connie Senior, Reaction Engineeering International

John Shepherd, University of Southampton

Thomas Spiro, University of Washington

Aldo Steinfeld, Eidgenössische Technische Hochschule Zürich

Handan Tezel, University of Ottawa

Frank Zeman, New York Institute of Technology

Guests at Princeton Workshop
March 23-25, 2009

Elie Bou-Zeid, Princeton University

William F. Brinkman, Princeton University, former committee co-chair, now head of the Office of Science, U.S. Department of Energy

Anthony Cugini, U.S. Department of Energy

Peter Eisenberger, Columbia University

Nathan Gorence, National Center for Energy Policy

David Keith, University of Calgary

Peter Kelemen, Columbia University

Klaus Lackner, Columbia University

Sau-Hai (Harvey) Lam, Princeton University

Arun Majumdar, University of California at Berkeley, former committee co-chair, now head of Advanced Research Projects Agency-Energy (ARPA-E), U.S. D.O.E

George Richards, U.S. Department of Energy

Francis Slakey, American Physical Society

Josh Stolaroff, U.S. Environmental Protection Agency

Michael C. Trachtenberg, Carbozyme

Frank Zeman, New York Institute of Technology

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