Perspective

Toward Transformational Carbon Capture Systems

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Introduction

Since the industrial revolution, fossil energy has promoted economic growth, and this has led to widespread prosperity. It has also significantly increased the concentration of CO_2 in the atmosphere. Continued CO_2 emissions pose a significant global threat. According to the United Nations Intergovernmental Panel on Climate Change (IPCC), atmospheric concentrations of CO_2 equivalent must be limited to 450 ppm by 2100 to prevent global warming of greater than 2°C.[1] One approach to reducing CO_2 emissions is to couple carbon capture and storage (CCS) technology with fossil energy systems. Other approaches include increasing energy efficiency and increases in the use of nuclear, wind, solar, and bioenergy. The IPCC evaluated a number of potential scenarios with various combinations of these approaches and showed that when used together, they could limit global warming to 2°C.[1] However, without CCS as an option, less than half of the scenarios were successful, and those that were successful were 138% more expensive on average.[1] Thus, CCS is critical to limiting atmospheric CO_2 concentrations in a cost-effective manner.

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The immediate, direct costs associated with the deployment of CCS technology have been a barrier to wide-scale deployment of the technology. While new carbon capture technologies may decrease those costs over time, in the near term, without strong policy and regulatory drivers to globally encourage the adoption of greenhouse gas (GHG) mitigation technologies, there exist limited incentives for industry to deploy the existing state-of-the-art (SOTA) technologies for CCS.

To overcome this impasse and enable a path such as that shown in Figure 1, where CCS from stationary point sources contributes to a 14% cumulative carbon dioxide emission reduction through 2050, requires the rapid development of new, transformational carbon capture technologies. In addition to exhibiting significant cost reductions, these transformational carbon capture technologies must also be ready for first-of-a-kind (FOAK) commercial-scale demonstration projects to be operational by 2025. Because the concept of CCS was first suggested as a potential approach for mitigating global change nearly 40 years ago,[2] a radical new approach to technology development must be pursued to meet U.S. Department of Energy (DOE) goals to enable the widespread commercial deployment of second-generation and transformational carbon capture technology to begin in 2030 and 2035, respectively.

In this article, we briefly review the history and current state of CCS research and development (R&D) and describe the technical barriers to carbon capture. We argue forcefully for a new approach to R&D, which leverages both simulation and physical systems at the laboratory and pilot scales to more rapidly move the best technologies forward, prune less advantageous approaches, and simultaneously develop materials and processes.

Background of CCS R&D

Although the concept of CCS was first suggested in 1977,[2] initial U.S. research efforts did not begin until the early 1990s.[4] An early assessment of CCS identified fossil-fuel-fired

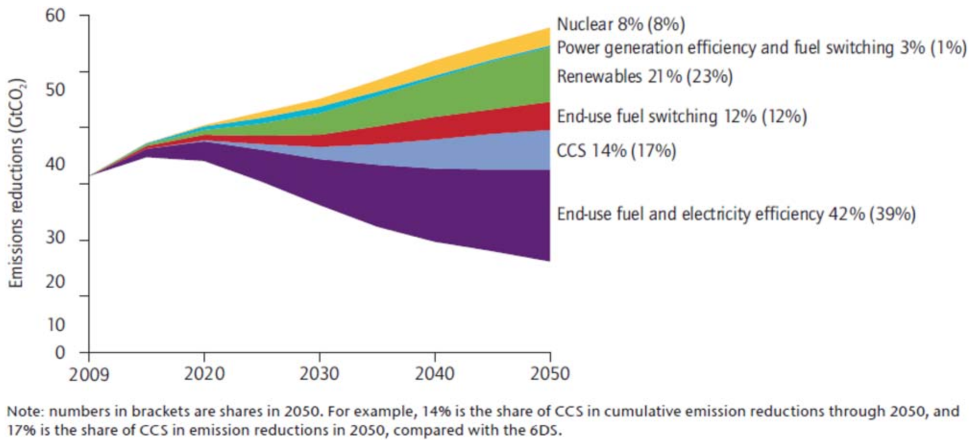


Figure 1. IEA graphic showing the contributions of different technologies in the achievement of the target emission reduction level in gigatonnes of CO_2 ($GtCO_2$) for the 2 degree scenario compared with the 6 degree scenario (6DS).[3]

electric power plants as a major point source of CO_2 and drew the following conclusions, many of which are still applicable today:[5]

1. The implementation of CO_2 capture and sequestration on a national scale will decrease power plant net efficiencies and significantly increase the cost of electricity (COE). To make responsible societal decisions, accurate and consistent economic and environmental analysis of all alternatives for atmospheric CO_2 mitigation are required.
2. Commercial CO_2 capture technology, although expensive and energy intensive, exists today.
3. The most promising approach to more economical CO_2 capture is the development of power plant systems that facilitate efficient CO_2 capture.
4. Although CO_2 disposal in depleted oil and gas reservoirs is feasible today, the ability to dispose of large quantities of CO_2 is highly uncertain because of both technical and institutional issues. Disposal into the deep ocean or confined aquifers offers the potential for large-quantity disposal, but there are technical, safety, liability, and environmental issues to resolve. Therefore, the highest priority research should focus on the establishment of the feasibility of large-scale disposal options.
5. Land or ocean disposal will require research to better understand environmental impacts. Even with such information, the public may be reluctant to accept some disposal options.
6. While the transportation of compressed, liquid CO_2 has been demonstrated, important issues involving cost, safety, liability, and institutional barriers to large-scale deployment remain.
7. Individual options for using captured power plant CO_2 in an alternate fuel, as an industrial feedstock, or as an agricultural growth enhancer are not promising for the sequestration of significant amounts of CO_2.

The previous conclusions have been the basis for approximately 2 decades of research related to CCS. Items 4-5 motivated a broad program in carbon sequestration to provide the scientific and technical basis for large-scale adoption, including the determination of storage capacity,[6] the investigation of reservoir-injection dynamics, and long-term monitoring. The DOE conducted this work through two major initiatives, the Regional Carbon Sequestration Partnerships Program[7,8] and the National Risk Assessment Program.[9] Recently, a significant milestone was reached with the safe injection of over 10 million tons of CO_2 into underground storage reservoirs through the regional partnerships and the DOE major demonstrations program.[10]

Although item 2 suggested that commercial CO_2 capture technology existed in 1993, it was prohibitively expensive and had never before been deployed on the scale necessary for a power plant. Such technology is now typically referred to as first-generation technology. In the case of postcombustion capture, this is typically based on aqueous amines. In the case of precombustion capture, this is typically either based on Selexol™ or Rectisol®. Only recently has CCS reached the milestone of applying postcombustion carbon capture technology to coal-fired flue gas on an industrial scale with the 2014 commissioning of Sask Power's Boundary Dam CCS demonstration system.[11] In many ways though, the costs still remain too high.

Conclusions 1 and 3 provided an incentive for the development of new, less energy-intensive approaches for capturing CO_2 from power plants. In addition to technologies directly related to the separation of CO_2 from flue gas or other effluent streams, this has included research to develop more efficient advanced energy systems to reduce the carbon intensity of power generation. These systems include the integrated gasification combined cycle (IGCC) and ultrasupercritical pulverized coal (PC) power plants, which have higher overall thermal efficiencies as well as oxycombustion systems, which change the nature of the separation problem. A related approach, chemical looping, tightly integrates energy conversion with carbon capture.[12] Many analyses of these approaches have been investigated over the past 20 years, and they are summarized in the IPCC reports [13]

There continues to be great enthusiasm for IGCC as a cost-effective route to advanced, low-carbon fossil energy because early analyses indicated that IGCC with CCS was among the most cost-effective options, even though IGCC itself is more expensive than PC for power production.[14] Furthermore, IGCC has the potential to be both a power generation platform while providing added flexibility to manufacture other high-value energy commodities, including transportation fuels and petrochemicals. More recent analyses have indicated that ultrasupercritical PC power plants have a similar COE with 90% carbon capture and a much lower capital cost for the base power plant.[15] Thus, with the additional incentive of the large installed base of combustion-based power plants, considerable emphasis has been focused on the development and scale-up of technologies for postcombustion capture (PCC). The development and deployment of PCC technologies will yield the largest impact on the reduction of the cost of CO_2 capture and will provide a technological solution to a large portion of the current power sector sources responsible for a majority of the CO_2 emissions globally.

Recommendation 6 regarding pipelines for CCS has not received as much attention because it is considered a commercially available technology in the United States, as demonstrated by the extensive CO_2 pipelines used for enhanced oil recovery (EOR). Finally, despite the strong statement of recommendation 7, new concepts for CO_2 utilization continue to be developed to offset a portion of the costs of CCS. These new concepts include mineralization and the use of CO_2 as a feedstock or feedstock blend for fuel production or as a feed to enhance biological growth (i.e., algae).

DOE Carbon Capture Program

At this time, PCC is the main focus of the DOE Carbon Capture Program. Nearly all of the existing coal- and natural-gas-generating capacity in the United States would directly benefit from the PCC technologies being developed. In addition, PCC is directly applicable to many other types of point sources, such as refineries and cement manufacturing. As of 2013, there were over 300 GW of coal-fired generation capacity and over 450 GW of installed natural-gas-fired capacity in the United States.[16] A majority of this 750 GW of combined generating capacity could retrofit their facilities with the technologies being developed by the DOE. In addition, coal-fired power plants being repowered and new coal- and gas-fired power plants in the United States and abroad (including those in developing countries, such as China and India) will directly benefit from these technologies.

The cost of CCS is still too expensive to promote widespread deployment without external regulatory drivers, such as those recently finalized by the U.S. Environmental Protection Agency (EPA) under sections 111(b) and 111(d) of the Clean Air Act for both new and existing power plants, respectively. These rules constitute the Carbon Pollution Standards, which set emission standards for new sources, and the Clean Power Plan, which sets statewide emissions caps for existing sources. The EPA also states that CCS can be considered a compliance option for existing sources to reduce GHG emissions under 111(d). The final 111(b) regulations for new power plants set the emissions standard at 1400 lb. CO_2/MWh gross for coal-fired power plants and 1000 lb. CO_2/MWh gross for natural-gas-fired power systems. Under 111(b), the EPA states that CCS is the Best System of Emissions Reduction for coal plants. The 111(b) rule requires a new SOTA PC-fired power plant to capture approximately 16% of its CO_2 emissions.[17,18]

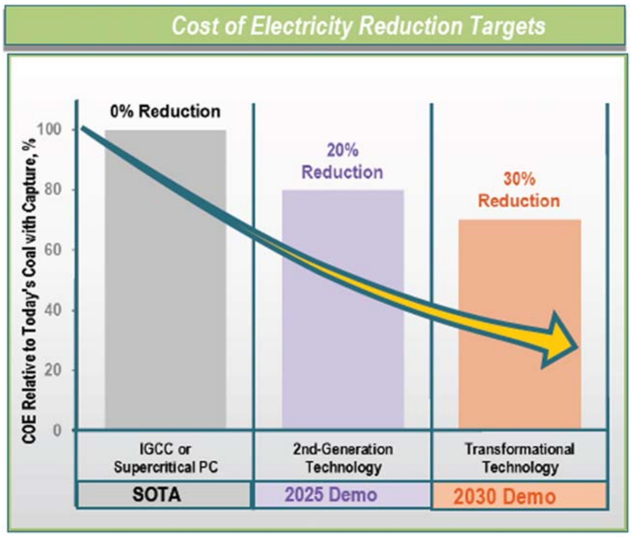
In addition, the U.S. Government has provided incentives, such as tax credits for carbon dioxide sequestration and a loan guarantee program, to support the commercial demonstration of advanced power generation and CCS. The Administration's 2016 budget to Congress requests to increase in the credit for storage in saline formations to $50/metric ton and to expand the total available tax credits to $2 billion.[19] Many U.S. states have also taken action to incentivize CCS by setting portfolio standards that include the generation of electricity from power plants with CCS, including generation with CCS as part of alternative fuel standards, prioritizing CCS during power plant permitting processes, providing various tax incentives, and providing cost recovery through authorized rate changes for power plants with CCS. International countries and some non-governmental organizations (NGOs) have also begun to adopt policies and nonbinding resolutions to reduce GHG emissions, which will open potential markets to vendors developing technologies for carbon capture. Because of the global nature of climate change, the December 2015 Conference of the Parties to the United Nations Framework Convention on Climate Change in Paris will define an international framework for carbon reductions, where CCS will certainly play an important role.

Even with such regulatory drivers and government incentives, it is important to reduce the cost of CCS to support its deployment and to minimize its economic impact. The cost for a next of a kind plant with today's SOTA postcombustion carbon capture technology is estimated to be $56/ton of CO_2 captured (2011 dollars, not including transport and storage) and represents an increase in the COE of approximately 62% over an uncontrolled plant. However, the estimated cost may not fully account for the unique cost premiums associated with the initial, complex integration of emerging technologies in a commercial application.[15] Over 75% of the total cost of CCS arises from carbon capture and compression; thus, it is imperative to develop new technologies to reduce the total cost of CCS to enable its widespread deployment.

To help reduce these costs, the DOE is pursuing a three-pronged approach, which includes

1. Large-scale, major demonstrations to address integration issues. Although these are based primarily on first-generation technology, the knowledge gained at scale can often be transferred to more advanced capture technology and provide increased confidence for deployment.
2. Development and pilot-scale testing of second-generation technology, which use new materials to incrementally reduce energy and capital requirements with largely conventional processes based on solvents, membranes, and solid sorbents. The pilot-scale testing uses actual flue gas to ensure that the capture materials do not undergo significant degradation in the presence of other pollutants in the flue gas.
3. Development of new, transformational technologies, which seek to use radically new approaches to significantly reduce costs.

Such advances in PCC, when paired with base plant improvements (e.g., advanced power cycles), are targeted to



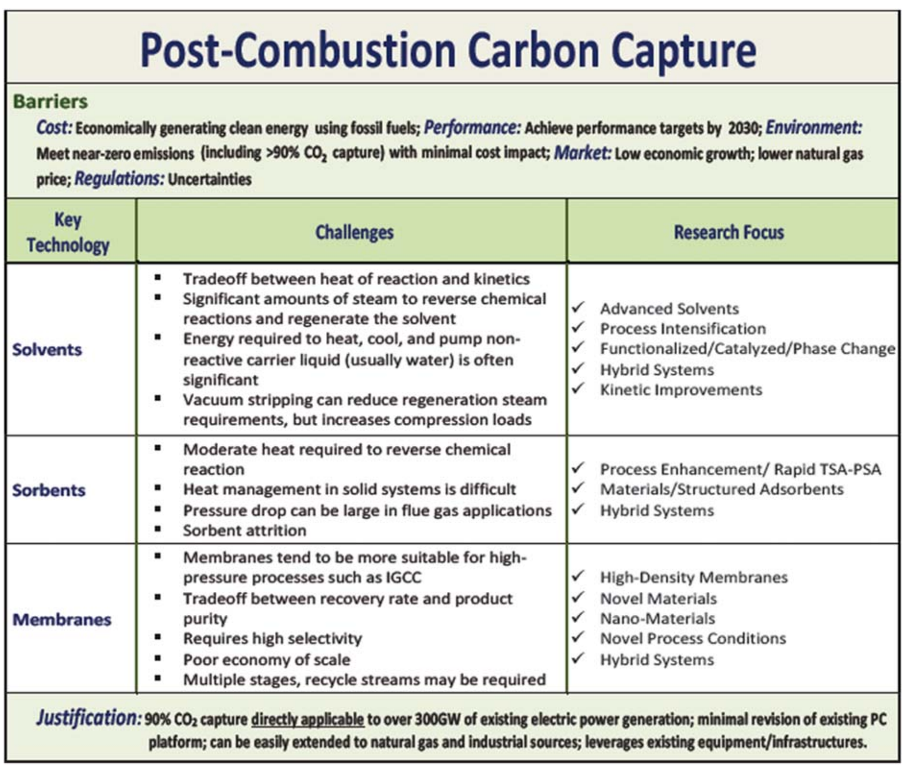
Goals shown are for greenfield plants. Costs include 90% CO_2 capture and compression to 2215 psia but exclude CO_2 transport and storage costs.

Figure 2. DOE roadmap for cost reduction in the progress of carbon capture technology.

meet DOE's cost goals for greenfield coal plants with 90% CO_2 capture, as shown in Figure 2. These goals are based on both technology and market considerations and were selected based on examination of the following: (1) comprehensive cost and performance assessments of SOTA power systems with CCS, (2) cost and performance assessments integrating advanced technologies into power plants with CCS for multiple combustion- and gasification-based configurations, (3) technology readiness levels of advanced technologies and associated projections for commercial readiness, and (4) market analyses to assess competitiveness of the proposed goals in various carbon-constrained scenarios within the timelines proposed. Figure 3 summarizes the specific challenges that are being addressed by research on second-generation and transformational PCC technologies.

Overall, the DOE's Office of Fossil Energy is providing R&D funding for over 60 individual projects investigating a wide variety of CO_2 separation techniques and the development of advanced processes and related components to support these new separation technologies and to improve the efficiency of capture systems. It has become clear that integrating the various advanced processes and components with advanced separation technologies in different combinations will be necessary to reduce the costs to levels which will make power plants with CCS competitive with other sources of electric power generation.

The Major Demonstration Program currently has seven projects that include both power and industrial applications. The Leucadia, Air Products, and Archer Daniel Midland projects capture CO_2 from industrial operations that produce methanol, hydrogen from steam methane reforming, and ethanol, respectively. The Hydrogen Energy California (HECA), Southern Co.-Kemper, and Summit projects are based on precombustion capture from IGCC facilities. Petra Nova is demonstrating second-generation PCC based on the KM CDR Process®.[21] Cost and large-scale integration issues remain at the forefront of the technical challenges associated with these large-scale demonstrations.



Post-Combustion Carbon Capture

Barriers

Cost: Economically generating clean energy using fossil fuels; *Performance:* Achieve performance targets by 2030; *Environment:* Meet near-zero emissions (including >90% CO_2 capture) with minimal cost impact; *Market:* Low economic growth; lower natural gas price; *Regulations:* Uncertainties

Key Technology	Challenges	Research Focus
Solvents	▪ Tradeoff between heat of reaction and kinetics ▪ Significant amounts of steam to reverse chemical reactions and regenerate the solvent ▪ Energy required to heat, cool, and pump non-reactive carrier liquid (usually water) is often significant ▪ Vacuum stripping can reduce regeneration steam requirements, but increases compression loads	✓ Advanced Solvents ✓ Process Intensification ✓ Functionalized/Catalyzed/Phase Change ✓ Hybrid Systems ✓ Kinetic Improvements
Sorbents	▪ Moderate heat required to reverse chemical reaction ▪ Heat management in solid systems is difficult ▪ Pressure drop can be large in flue gas applications ▪ Sorbent attrition	✓ Process Enhancement/ Rapid TSA-PSA ✓ Materials/Structured Adsorbents ✓ Hybrid Systems
Membranes	▪ Membranes tend to be more suitable for high-pressure processes such as IGCC ▪ Tradeoff between recovery rate and product purity ▪ Requires high selectivity ▪ Poor economy of scale ▪ Multiple stages, recycle streams may be required	✓ High-Density Membranes ✓ Novel Materials ✓ Nano-Materials ✓ Novel Process Conditions ✓ Hybrid Systems

Justification: 90% CO_2 capture directly applicable to over 300GW of existing electric power generation; minimal revision of existing PC platform; can be easily extended to natural gas and industrial sources; leverages existing equipment/infrastructures.

Figure 3. Postcombustion carbon capture challenges.[20] TSA and PSA refer to temperature swing adsorption and pressure swing adsorption, respectively.

Table 1. Summary of Carbon Capture RD&D Timelines

	Second generation	Transformational
R&D completed through large-scale pilot testing (10-25 MWe)	2020	2025
Permitting and construction of FOAK demonstration projects (100+ MWe)	2020–2025	2025–2030
Startup of commercial-scale FOAK demonstration projects initiated	2025	2030
Commercial deployment begins	2030	2035

Second-generation carbon capture technologies currently under development, including base plant improvements, are expected to result in a 20% reduction in the COE or better relative to SOTA technology for new, greenfield plants; this cost reduction is equivalent to a capture cost of \$40/ton of CO_2, not including transport and storage.[22,23] CCS technologies for retrofitting existing plants will be critical both for U.S. and global CO_2 mitigation goals. The retrofitting of second-generation CCS technologies to existing PC plants will become financially feasible for a portion of the U.S. fleet by selling CO_2 for EOR and/or economic incentives to reduce CO_2 emissions. R&D (through large-scale pilots) for second-generation technologies is targeted to be completed by 2020 with the startup of commercial-scale demonstrations in 2025, as summarized in Table 1.

In the long term, the development of transformational technologies is required to create systems that can achieve widespread market deployment. These systems will ensure cost-competitive fossil units with options for CO_2 disposition beyond EOR. Only through the pursuit of disruptive concepts can the additional reductions in COE and cost of capture beyond second-generation targets be achieved. This requires breakthrough research, development, and demonstration (RD&D) that can provide a total of a 30% reduction in the COE or better relative to SOTA technology.[22,23] The study of the ultimate and practical performance limitations of candidate transformational technologies is just now beginning; a quantified metric adhering to these constraints is expected to be available in 2016 as the DOE revises its R&D Pathways study. Although the economic deployment of transformational retrofit technologies to the existing U.S. coal fleet may be limited as it ages, there will be substantial opportunities for transformational technology to be applied to new coal-fired power plants, international coal CCS retrofits, and Natural Gas Combined Cycle (NGCC) CCS retrofits. Transformational R&D is targeted to be complete by 2025, with the startup of FOAK demonstration plants between 2025 and 2030 and widespread commercial deployment beginning by 2035.

There are several major challenges that must be overcome in the advancement of technologies from first generation to transformational, as shown below.

1. *Cost effectiveness*: Current carbon capture technologies are expensive and energy-intensive. This results in a COE increase of approximately 75–80% and a cost to capture CO_2 of nearly double what it can be sold for in today's EOR market. Reducing both these costs to practical levels is a significant challenge.
2. *System integration*: In most cases, integrating the CO_2 capture subsystem with the balance of plant will increase operational and thermodynamic efficiency; however, the cost and complexity associated with this integration represents a significant barrier.
3. *Scale-up*: Although industrial-scale CO_2 separation processes are now commercially available, they have not been deployed at the scale required for large power-plant applications. As these technologies advance, integration with the balance of plant is likely to become more complex. Addressing deployment and integration issues at relevant scales is essential for minimizing low-carbon power production costs.
4. *Supply chain*: The current gas-processing and gas-separation industry would need to be scaled at least an order of magnitude from today's capacity. The increased scale will put strains on the commodities needed for solvent, sorbents, and membranes as well as the more conventional equipment vendors that will need steel and other commodities.
5. *Thermodynamics*: In most cases, CO_2 is present along with significant amounts of other gaseous constituents, which reduces the driving force for separation from flue gas and increases the thermodynamic cost of separation.
6. *Parasitic load*: A significant amount of auxiliary power is required to operate currently available CO_2 capture technologies. The auxiliary power decreases the net electrical generation of the power plant.
7. *CO_2 compression*: For most CO_2 disposition options, significant power is required to compress the captured CO_2 to pressures at which it can be stored or utilized. Reducing of this power requirement helps to improve overall plant efficiency and facilitate CO_2 storage for both existing and future power plants.
8. *Flue gas contamination*: Constituents in the flue gas, particularly sulfur, can contaminate CO_2 capture technologies, leading to increased operational expenses.
9. *Water use*: Depending on the technology, a significant amount of water may be required for CO_2 capture and compression cooling.

Accelerating the Discovery of Transformational CO_2 Capture Concepts

Over the past several decades, investments across the DOE in high-performance computing and materials characterization, synthesis, and manufacturing have created a foundation for the development of new technologies that can solve the GHG emission challenge. The DOE National Laboratories and U.S. research universities have been the recipients of much of this investment, utilizing these tools to advance scientific understanding and discovery as well as to develop specific technology solutions. A number of research groups are currently focusing their efforts on materials concepts that represent evolutionary advances in membranes, sorbents, and advanced processes for fossil and other clean energy systems. In almost all cases, the focus is on the development of high-performance materials that exhibit a few targeted characteristics, without *a priori* consideration of the real requirements that will be put on the material in application or the real costs associated with their implementation. What is generally missing in this approach is a holistic view of materials development, which incorporates an optimization step (or steps) that considers the material's performance in the context of a real, thereby enabling the development and utilization of truly transformational capture materials in a functional capture system.

Affordable, transformational carbon capture technologies are likely to be invented by holistically coupling of the enormous possibilities of new materials (e.g., ionic liquids, metal-organic frameworks, or materials yet to be discovered) with capture processes that are engineered to exploit the material's favorable properties while overcoming negative ones. However, the identification of new materials poses a significant challenge to researchers due to the polydimensional nature of materials design, where design criteria, including components (periodic table), composition (elementally complex), structure, phase, and morphology (countless variability), pose possibilities greater than can be comprehended. This challenge is compounded further when material performance needs to span scales covering orders of magnitude and translate to service life and economics, often in very complex systems or environments.

To address these challenges, a top-down virtual environment to engineer new carbon capture materials with tailored properties needs to be integrated with experimental capabilities to rapidly synthesize and test materials as well as advanced manufacturing techniques to functionalize these materials while being driven by the requirements of the large-scale process. Such integration will require bringing the separations industry into a research partnership that convenes the "best of the best" across the National Lab complex and university system in conjunction with industry, which will provide validation for projects and key activities, help determine process performance requirements, and establish a path for commercialization. The primary goals of such an initiative will be to coordinate and execute a body of research to

- *Utilize advanced computational tools* for virtual materials design and discovery that will reverse-engineer disruptive materials in a virtual environment focused on higher scale requirements (i.e., process driving device, device driving material performance, material performance driving material design).
- *Synthesize materials and test performance* through experimentation and characterization for model validation.
- *Functionalize and fabricate* promising materials into systems and devices with advanced manufacturing that can be demonstrated under real conditions and at scale.

Screening new concepts

Many novel or transformational CO_2 capture concepts have been identified for consideration. These include advanced solvents, electrochemical systems, cryogenic systems, phase-change solvents, and various hybrid systems. All have shown technical promise, while still having technical hurdles to overcome. With limited resources to pursue all possible technologies, it is critical to have a systematic approach for screening technologies. The screening must take into account both the performance and likely cost, but more importantly, it must help to determine the ultimate process. As noted previously, a truly transformational CO_2 capture concept is likely to incorporate multiple advanced technologies. Thus, a framework for evaluating new concepts must enable the potential integration of multiple technologies and do so in a way that can optimize the entire system.

Another challenge that occurs during screening concepts is estimating the cost of an *n*th-of-a-kind plant with entirely new technology. It is likely that until the *n*th plant is actually built, the level of uncertainty in any cost estimate will be very high.[24] For that reason, it is essential that cost estimates used for screening be open to scrutiny and performed on a common basis with all of the assumptions, factors, and methods clearly documented.[25]

Additional factors also need to be considered during the screening of potential transformational CO_2 capture technologies because of the timeline involved. There needs to be a credible path to demonstrate the technology at pilot scale within 10 years (i.e., by 2025). Thus, if a potentially disruptive material has just been identified, and its only method of production will require 10 times the world's supply of a critical material, it is unlikely to be viable. Other aspects of the complete life cycle for the materials proposed for the technology must be evaluated to ensure that a supply chain is possible and that byproducts, starting material, and so on do not pose unacceptable health or environmental risks.

One way to improve the screening of new concepts is to more rigorously integrate the use of science-based models into the development process. In the early stages, the establishment of standards for laboratory-scale data, acquired under appropriate conditions, would enable the development and validation of predictive models. Ideally, the use of such science-based models would become an integral part of a rigorous technology readiness assessment process.[26]

Computational Tools to Accelerate Transformational Concepts

In 2010, the DOE initiated the Carbon Capture Simulation Initiative (CCSI) to help reduce the amount of time that it historically takes to develop and scale up new technologies in the energy sector, where it traditionally takes up to 15 years to move from the laboratory to predeployment and another 20-30 years for industrial-scale deployment. As discussed previously, to maximize the impact of transformational carbon capture technology, it needs to be demonstrated at pilot scale within 10 years to enable commercial deployment to begin in 2035. Thus, it is imperative that such R&D activities leverage advanced modeling and simulation to enable rapid progress and help ensure success.

CCSI has developed and deployed a suite of multi-scale and multi-physics computational tools that are accelerating the development cycles of capture technologies based on solid sorbents and advanced solvents. Overall, this CCSI toolset (1) enables promising concepts to be more quickly identified through rapid computational screening of processes and devices, (2) reduces the time to design and troubleshoot new devices and processes with optimization techniques to focus development on the best overall process conditions and with detailed device-scale models to better understand and improve the internal behavior of complex equipment, and (3) provides quantitative predictions of device and process performance during scale-up based on rigorously validated smaller scale simulations that take into account model and parameter uncertainty.[27]

Tightly coupling modeling and experimental development offers significant benefits; however, it also requires a different approach to scale-up. Instead of following the often common goal of getting to the next scale as fast as possible, moving to the next scale can instead be determined based on the need for data that are not possible to collect on a smaller scale. Thus, it may be advantageous to continue collecting bench-scale data to obtain a richer set of data, which in turn enable a more predictive model, which could lead to a more successful pilot project. Developing and validating models can thus save money by ensuring that projects collect the data that they really need at the smallest scale possible.

As the CCSI team works with industry to support the scale-up of various carbon capture systems, a common theme has been the need to collect more data at the laboratory scale to create a predictive model that can actually assist with scale-up. Well-developed models can also help guide experiments to identify where simple experimental data is needed to enable prediction of behavior at scale.

Multi-scale models and validation

Models that predict device and process behavior are actually a series of models that are linked together. These submodels represent physical properties, thermodynamics, chemical reactivity, heat transfer, hydrodynamics, mass transfer, and other aspects of the device/process. Oftentimes, these submodels can be hidden from the user of a macroscopic model (e.g., a model for an absorber); however, the reliability of the overall model is highly dependent on the predictive capability of all of the submodels. Thus, it is essential to rigorously calibrate and validate both the underlying submodels and the overall model to ensure that it can accurately represent the physical system.

Parameters for submodels are typically calibrated deterministically for each submodel, which causes a number of issues. Both models and experimental data are imperfect. Thus, given experimental error, a number of sets of parameters can represent experimental data equally well. By taking only the "best fit" set of parameters, the submodel may not be able to represent the true behavior. When multiple submodels are combined together into an aggregate model of a process or device, these errors can multiply, resulting in poor predictive capability. Submodels are often coupled with one another. Thus, if the parameters of one submodel are determined in isolation from the related submodels, the regressed value of the parameters of the second submodel may be far from the "true" values.

It is essential that sufficient experimental data be available to cover the range of conditions over which the model will be used. Sometimes, submodels unknowingly extrapolate because prebuilt submodels are used from within commercial simulation packages without thoroughly investigating the data and assumptions that went into the model. Other times, inadequate data are used during the development of the model because it is difficult to measure the properties under those conditions. Ultimately, this can be a critical oversight causing the overall model to perform poorly if the submodel is extrapolating well beyond the range of conditions under which it was developed.[28]

Process models provide a balance between model accuracy and computational efficiency to enable simulation of an entire, integrated process. Although process models need sufficient rigor to accurately describe the behavior of CO_2 capture systems over wide ranges of operation, they must have sufficient computational tractability to enable their use for process optimization and for developing advanced process control strategies. Even though the limiting mechanisms often occur at lower spatial scales, process behavior is observed at much larger scales. Thus, it is often difficult to determine the root causes for model deficiency. In addition, determining what information should be passed between different scales is challenging. Some phenomena occur at very short timescales, whereas others occur at much longer timescales. Capturing these multiscale phenomena is very important for process models to be used for scale-up analysis. A thorough understanding of the key physical and chemical mechanisms that occur over these spatial and temporal scales is essential for developing accurate models.

The development and validation of device-scale modeling capabilities for advanced capture technologies are critical in reducing the time and cost of scale-up and process optimization. Since most advanced carbon capture concepts have multiphase reactors at the core of the system, multi-physics device-scale models that solve spatially dependent coupled CO_2 capture reactions along with heat transfer and hydrodynamics for a given reactor geometry are essential for bridging the predictive confidence between laboratory-scale, pilot-scale, and plant-scale behavior of a process.

Model calibration is an important component of model development which helps to estimate the most likely values of model parameters that cannot be estimated from existing correlations, mechanistic or phenomenological models, nor from first principles. Models must be validated so that sufficient trust in them can be built before advancing to the next scale. In addition, model validation can be instrumental in identifying model deficiencies due to lack of knowledge of the physics and chemistry of the process or due to the inability to model them accurately.

High-quality validation data from CO_2 capture technology as it transitions from one scale to the next is rare; however, such data, including dynamic behavior, are essential. The transient response of a process provides hundreds of data points in response to a change in an input in contrast to a single value if only steady-state conditions are considered. Although steady-state responses can be arbitrarily fit to many nonunique combinations of model parameters, nonlinear transient response enables better model calibration to minimize the uncertainty associated with a model. Such studies can also identify whether important mechanisms are being neglected.

To overcome these issues, CCSI developed a comprehensive, hierarchical model calibration and validation framework, which uses Bayesian statistics and other principles of uncertainty quantification, to provide stochastic model predictions that result in a complete probability distribution of expected behavior.[29–32] This is especially important when using models to help predict scale-up performance since it enables confidence bounds to be placed on simulation results. Furthermore, the sensitivity of the model's predictions to uncertainty in specific submodels and parameters can be determined. This allows technology developers to focus additional resources on those aspects of their process that have the biggest influence on uncertainty, which is closely related to technical risk.

Modeling in conjunction with large-scale pilots

Several second-generation carbon capture technologies are already being demonstrated at the small pilot scale (1 megawatt electric, MWe). As they move to larger scales, the financial investment and risk to the government and industrial partners begin to increase substantially. The use of detailed, validated models can help ensure success and minimize risk, as these technologies move toward demonstration scale; however, it is critically important to partner modeling experts with technology developers at the beginning of a scale-up project to ensure that the right data are collected and the right experiments are conducted at the current scale to enable prediction at the next scale with quantitative confidence. The DOE established a successor program to CCSI called Carbon Capture Simulation for Industry Impact ($CCSI^2$), which is planned to provide such a partnership with the developers of several large-scale pilot projects for second-generation capture technologies. These partnerships will ensure that the full benefits of intermediate-scale projects are reaped by the larger scale projects.

DOE issued a Funding Opportunity Announcement (FOA) at the beginning of 2015 to seek applications to test second-generation carbon capture technologies at a large pilot scale (10+ MWe).[33] Awards from Phase 2 of this FOA are expected by September 30, 2016, with at least two technologies being selected to construct and operate their second-generation systems through 2020. These large-scale pilots represent the last scale before commercial-scale demonstration of the technologies. It is expected that these systems will be component technologies and not be fully integrated with the power plants that host them. The results of these projects will provide data on materials and capture-system performance. The information gathered from these pilot projects could be used in conjunction with $CCSI^2$ to determine the optimal process configuration for a commercial-scale demonstration facility, which would ready for startup by 2025.

The approach will include the development and application of basic data submodels, process models, and device models as necessary to represent the physics of the carbon capture technologies. The resulting suite of multi-scale models will inform technology developers about data requirements to enable full validation of the models so that they can be used to predict system performance during further scale-up. In addition, the resulting models will be used to help improve, optimize, and integrate capture technology during further development. Finally, the models will help ensure the success of the large-scale pilots by providing the ability to better understand the dynamic behavior of the system before the test units are built and to help troubleshoot issues that arise during testing.

Conclusions

CCS is critical for reducing atmospheric CO_2 concentrations, and the costs of limiting the rise in the average global temperature by 2°C are significantly higher without the use of CCS. Despite this long-term economic incentive for CCS, the short-term economic costs limit its widespread deployment and hamper efforts to establish policy and regulatory drivers that would incentivize deployment. In order to overcome these barriers, it is essential that transformational capture technologies be developed that reduce the cost significantly. Such transformational technologies will reduce the negative economic impact of deployment while also reducing resistance to implementing regulatory drivers.

However, the timeline to get transformational CO_2 capture technology ready for commercial demonstration at the 100+ MWe scale is remarkably short—only 10 years to avoid significantly increasing the lifetime costs associated with reducing atmospheric CO_2 levels. Thus, it is essential that R&D for transformational carbon capture technology be conducted in a more holistic manner, tightly coupling experimental development with modeling and simulation, incorporating advanced manufacturing and involving more stakeholders (utilities, technology providers, material suppliers, etc.) earlier in the process. More effort needs to be made to obtain the right data at the right scale. Moving to larger scales faster is not necessarily a sign of progress if the fundamental understanding has not yet been developed. Instead, a technology should only progress to a larger scale when questions arise that cannot be answered at a smaller scale. A rigorous maturation process can help ensure that technology transitions occur at the right time. Ultimately, these new technologies will need to be demonstrated at the pilot and demonstration scales; however, if researchers spend more time initially at a small scale, gaining understanding and validating models, larger scale projects can progress with lower risks and a higher probability of success.

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