

Measurement, Standards, and Data Needs for CO₂ Capture Materials: A Critical Review

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S Supporting Information

ABSTRACT: The commercial deployment of cost-effective carbon capture technology is hindered partially by the lack of a proper suite of materials-related measurements, standards, and data, which would provide critical information for the systematic design, evaluation, and performance of CO₂ separation materials. Based on a literature search and conversations with the carbon capture community, we review the current status of measurements, standards, and data for the three major carbon capture materials in use today: solvents, solid sorbents, and membranes. We highlight current measurement, standards and data activities aimed to advance the development and use of carbon capture materials and major research needs that are critical to meet if innovation in carbon capture materials is to be achieved. The review reveals that although adsorbents are considered to have great potential to reduce carbon capture cost, there is no consensus on the experimental parameters to be used for evaluating sorbent properties. Another important finding is the lack of in situ experimental tools for the structural characterization of solid porous materials during CO₂ adsorption, and computational methods that would enable a materials-by-design approach for their development.



■ INTRODUCTION

Global emissions of carbon dioxide (CO₂) reached 34 billion tonnes in 2011, up 3% relative to 2010 and the highest level on record (This assessment includes fossil fuel combustion as well as other CO₂ emissions sources such as flaring of waste gas during oil production and cement clinker production and other limestone uses, feedstock and nonenergy uses of fuels and other small sources). Over the past decade, an average annual increase of 2.7% has been reported with the top five emitters being China (29%), the United States (16%), the European Union (EU27) (11%), India (6%), and the Russian Federation (5%).¹ If global increases in CO₂ emissions continue at this rate, it is anticipated that within the next two decades global CO₂ cumulative emissions will reach levels that will make it impossible to meet a critical, internationally agreed-upon target established in international climate negotiations² to hold the increase in global temperature below 2 °C.¹

The environmental impact of the increasing concentration of anthropogenic CO₂ in the atmosphere³ underlies the urgent need for carbon mitigation.^{2,4} This is well understood, by both the scientific⁵ and general public communities. For example, with respect to the latter point, the average U.S. citizen is willing to accept a 13% increase in electricity prices in support of a national clean energy standard.⁶ This is important in the context of greenhouse gas (GHG) emissions mitigation and the clean energy economy goals of the U.S. The primary domestic sources of energy in the U.S. are fossil fuels, with 42% from coal and 25% from natural gas in 2011.⁷ Coal currently accounts for

about 81% of CO₂ emissions from the U.S. electricity sector, which encompasses generation, transmission, and distribution of electricity per the U.S. Environmental Protection Agency (EPA).⁸ The EPA takes this very seriously and seeks to lessen atmospheric CO₂ emissions from this sector.⁹ While the EPA is promoting strategies to reduce fossil fuel consumption to make this happen (i.e., increasing energy efficiency and conservation, and encouraging fuel switching), carbon pollution standards for new power plants have been proposed in parallel¹⁰ as part of the EPA's efforts to reduce atmospheric carbon pollution under the purview of the Clean Air Act (see Table 1). EPA notes in its proposal for standards for power plants that it does not foresee the development of any new coal-fired electrical generating units (EGUs) without carbon, capture, and storage (CCS) technologies in the absence of its carbon pollution standards (CCS refers to the use of a technology for separating and capturing CO₂ from the flue gas or syngas stream with subsequent compression and transportation to a suitable location for long-term storage and monitoring. Many references include "sequestration" rather than "storage". EPA considers these to have the same meaning and the words are used interchangeably by the Agency). Further, units could meet the standard by employing CCS of approximately 50% of the CO₂

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Table 1. Selected Key Actions Taken by the U.S. EPA to Implement Clean Air Act Requirements for Carbon Pollution from Stationary Sources and CCS

title	purpose	relevant dates
proposed carbon pollution standard for new power plants	to set national limits on the amount of carbon pollution that new fossil-fuel-fired electric utility generating units can emit.	published April 13, 2012 ¹⁰
greenhouse gas tailoring rules	to set greenhouse gas emissions thresholds to define when permits under the New Source Review Prevention of Significant Deterioration (PSD) and Title V Operating Permit programs are required for new and existing industrial facilities. Step 1 and 2: initial thresholds set Step 3: retains thresholds established in Steps 1 and 2 plus additional elements to streamline the administration of PSD permits for GHGs.	Steps 1 and 2 published ⁸⁵ June 3, 2010; Step 1 effective January 2, 2011 to June 30, 2011 Step 2 effective July 1, 2011 to June 30, 2013 Step 3 published ⁸⁶ July 12, 2012 effective August 13, 2012
mandatory reporting of greenhouse gases	to collect greenhouse gas data from large emission sources across all sectors of the economy. Greenhouse gas data are available through the EPA greenhouse gas reporting program tool.	published October 30, 2009 ⁸⁷ effective December 29, 2009 ⁸⁸
geologic sequestration of carbon dioxide	to provide finalized requirements for geologic sequestration, including the development of a new class of wells, Class VI, under the authority of the Safe Drinking Water Act's Underground Injection Control Program	requirements: published December 10, 2010 ⁸⁹ effective January 10, 2011 announcement of class VI program published September 15, 2011 ⁹⁰

Table 2. Basic Functions of Standards for Products or Services¹⁷

function	purpose	example
quality or reliability	to specify acceptable performance along one or more dimensions	specification of a minimum level of performance such as the minimal acceptable lubrication attributes in an automobile engine
information exchange	to provide evaluated scientific or engineering information	measurement standards and test methods standards that are universally accepted (see text)
compatibility or interoperability	to specify properties of a product to work physically or functionally with complementary products within the product's system	a standardized interface between components of a larger system such as the usb
variety reduction	to limit a product to a certain range or number of characteristics	physical dimensions of a product such as the width between threads of a screw

in the exhaust gas at startup, or through later application of more effective CCS to meet the standard on average over a 30 year period. EPA's proposal underscores the critical dependency of the U.S. power sector on significant advances in CCS technologies and the need, now more than ever, for these to launch.

For the interested reader, the carbon capture primer in the Supporting Information briefly describes the different carbon capture options, which include postcombustion, precombustion, oxy-combustion, and capture from other industrial process streams (See Supporting Information Figures S1–S3). Other informative reading material can be found in ref 11, which presents a comprehensive review on CCS for large stationary sources. Modern advances in CO₂ capture technology are covered in ref 12. Further, a recent synopsis of CCS, existing technology, and demonstration projects is presented in ref 13, which is the current U.S. federal strategy to accelerate the commercial development and deployment of CCS.

Innovation in CCS technologies is difficult, particularly for power plant applications, because the demonstration of realistic CO₂ capture capacity demands with current tactics is limited. Cost is another impediment. Carbon capture represents the most energy intensive component of CCS with the largest cause of efficiency reduction being the energy required to regenerate the liquid amine solution used to absorb CO₂.¹⁴ Approximately 75% of the total cost of CCS is due to this requirement, and there are additional costs due to amine degradation and corrosiveness. Such a large energy penalty increases the cost of electricity by greater than 75%.¹⁵ Major advances in carbon capture technologies are needed to overcome such problems. In particular, advanced materials

with novel properties preemptively tailored to meet the future needs of the power sector, in the U.S. and abroad,¹⁶ are required.

Advanced materials encompass entirely new materials or existing materials with a fresh-take on their physical or chemical properties, in either case the resulting candidate materials for carbon capture must surpass the performance of legacy materials. Testing and evaluation of a candidate material's performance requires a well-developed suite of complex materials characterization methods. The physical and chemical properties of a candidate material must be fully understood. Cutting-edge measurement science, standards, and data are needed to assess materials characterization at the smallest scales. Suitable, well-characterized standard materials are of the utmost importance to gauge the quality and comparability of candidate materials' structures, properties, and performance among identical entities and between classes of entities. This article reviews measurements, standards, and data activities and research needs to support the development, testing, and evaluation of advanced materials applicable to carbon capture with a focus on solvent, solid sorbent, and membrane technologies. In some instances, these activities are fully developed and supporting the needs of CCS development, testing, and evaluation, whereas in others, research is underway to support the future development of advanced carbon capture materials.

■ THE FUNCTIONS OF STANDARDS

In the technology theater, a standard can be viewed as a construct that results from a collective line of reasoning among

producers and users of products or services and offer a balance among the requirements of users, the technologies of the market, and the checks put in place by government for the public benefit.¹⁷ In short, standards support four basic functions (i.e., reliability, information, exchange, interoperability, and variety reduction) to grow technology-based economies. Table 2 describes each of these functions, largely based on refs 17 and 18, accompanied by relevant examples of standardized products commonly used today (e.g., USB interfaces for electronic devices). Standard examples specific to carbon capture materials are presented in the last section of this paper.

Measurement standards are derived from fundamental standards that provide a common reference for a property of interest. In the most accurate form, these are declarable to the fundamental constants of the International System of Units (SI) and are provided entirely by government. These transfer to industry via a working standard in which the working standard is a piece of equipment calibrated against a basic standard to a specified level of accuracy. The groundwork to support the information exchange to industry must be conducted by an authoritative source such as a National Measurement Institute (NMI) (NMIs are government-established entities that exist in most industrialized nations. NMIs are responsible for establishing traceable and comparable national standards of measurements within the SI framework that are mutually acceptable to all NMIs. These efforts provide a technical foundation for agreements related to international trade, commerce, and regulatory affairs. By federal statute, the National Measurement Institute of the United States is the U.S. Department of Commerce National Institute of Standards and Technology (NIST)).

Measurement standards can also be in the form of standardized scientific and engineering data (critically evaluated and verified for accuracy by an authoritative source such as an NMI), standardized equipment calibration methods, or well-characterized (physically or chemically) samples that are traceable to the SI, such as Standard Reference Materials (SRMs). With respect to SRMs and GHGs, NIST recently produced new gas mixture SRMs representative of northern and southern hemisphere air to support the World Meteorological Organization (WMO) Global Atmospheric Watch (GAW) measurement and monitoring programs. Such standards provide the measurement traceability required by NOAA to maintain and calibrate, as the overseer, the world's largest global monitoring network for atmospheric greenhouse gas concentrations. NIST has a long history of supporting the measurements needed for climate greenhouse gas emission monitoring and climate change research carried out by other federal agencies carried out by the U.S. government.¹⁹ Ultimately, these measurement standards are vital for establishing emission baselines, monitoring compliance, and verifying performance of policies or project-based approaches to meet pollution reduction targets (NIST has selected standards-specific research activities to support carbon capture materials development and these are detailed later in this review. With respect to our counterpart NMIs, however, we surmise from our conversations with them and the carbon capture community and review of the literature that there are very few similar or complimentary activities at other NMIs. With that said, the Joint Research Center, the scientific and technical arm of the European Commission (EC), has led the EC's activity to identify the materials research needs for the large

scale deployment of CCS but a dedicated activities on materials is not yet established).

Test method standards, generally termed documentary standards, are another type of standard which supports information exchange. These specify uniform criteria and technical methods to enable comparisons among products, processes, and test results, and help reduce risks and transaction costs in product and service markets. Standards developing bodies (SDOs) establish documentary standards. SDOs can be national or international in scope and draw on a broad range of technical expertise from industry and government, including NMIs. A familiar example of international organizations is the International Organization for Standardization (ISO). ISO is based on a model of one vote for each country; generally the American National Standards Institute (ANSI) represents the United States and is responsible for its vote. There are also independent standards organizations such as ASTM International who develop and publish technical standards for international use, but do not use the model of one vote for each country. Rather, each technical expert, many from NMIs, may comment and vote. Other organizations set documentary standards that are highly technical and specific to an industry. For example, the American Petroleum Institute (API) annually updates current standards, creates new standards, and adopts back existing standards for the petroleum industry to meet equipment, materials, measurement, and safety needs of the industry. Documentary standards from these or other independent organizations may be incorporated by reference and become regulatory. With respect to carbon capture documentary standards development, ISO established in 2011 a technical committee (TC) to standardize activities in the field of CCS including design, construction, operation, environmental planning and management, risk management, and quantification and verification but this does not have any work items at the moment.²⁰ The TC has 16 member countries and 10 observing countries.

■ CARBON CAPTURE MATERIALS DEVELOPMENT

The removal of CO₂ from gas streams can be achieved using absorption, adsorption, membrane separation, and cryogenic processing methods. For a comprehensive account emerging CO₂ capture materials, see ref 21. Absorption (or solvent technology) has been the most widely used for removing CO₂ from medium to high pressure gas streams with low oxygen content (e.g., natural gas purification or H₂ recovery).²² More recently, pilot- and demonstration-scale projects have been reported where the CO₂ was recovered from natural gas treatment plants¹⁴ and fossil fuel-fired power plants²³ using solvents. Despite its widespread use in CO₂ removal from natural gas, conventional amine-based solvent mixtures have been deemed too energy intensive to be commercially deployed for carbon mitigation. The energy intensity is partially due to the large amount of water (a fluid with a large heat capacity) present in the formulation (close to 70% by weight), which is required to avoid serious corrosion issues. Research efforts to decrease the regeneration costs of carbon capture technologies often seek to reduce, replace, or eliminate the water diluent. Solid sorbents (also known as adsorbents) are emerging as an alternative solvent-less approach to reduce regeneration costs.^{21h} The presence of CO₂-philic functionalities on the surface of adsorbents eliminates the need for using an aqueous diluent to avoid corrosion. Membrane technology is also becoming an attractive option for reducing operating costs as

membranes eliminate the need for regeneration.²⁴ Although not economically attractive, the first generation solvent technology is considered mature enough to service a prospective CO₂ capture industry^{22b} while competing solid sorbent and membrane technologies are in the R&D stage.¹² As a result, researchers and chemical manufacturers continue to optimize the benchmark amine-based CO₂ scrubbing technology.^{22b} A proprietary hindered amine solvent being tested in a pilot-scale project at a 25 MW coal-fired power plant captures 0.15 Mt CO₂/yr.²⁵ Other solvents being considered include chilled ammonia,²⁶ ionic liquids (ILs),²⁷ and aminosilicones.²⁸ Current trends and challenges for the various types of solvent, adsorbent, and membrane carbon capture materials can be found in ref 21b.

Materials and Processes. Presently, improvements in materials and processes are needed to minimize the added cost of electricity (COE) production after incorporating CCS technology to a power plant.²⁹ The R&D targets for carbon capture, as established by the U.S. DOE National Energy Technology Laboratory (NETL), are: 90% capture efficiency and an added COE below 35% for postcombustion and oxy-combustion, and 10% for precombustion.^{29,30} The amount of CO₂ projected to be captured per year to meet these targets can be astonishingly large, which could have implications on the scale of the capture material required. For example, the U.S. has approximately five hundred average-sized conventional coal-fired power plants (500 MW), each of which generates approximately 4.4 Mt CO₂/yr, equivalent to a capture rate of 3.9 Mt CO₂/yr (or approximately 8.9×10^9 mol CO₂/yr) in order to meet the DOE target. A study reports that for a solid sorbent to be competitive with alkanomine solvents, the CO₂ capture capacity must be between 3 mol CO₂/kg sorbent to 6 mol CO₂/kg sorbent.³¹ Such figures indicate that, depending on the adsorption capacity and kinetics of adsorption/desorption, the amount of solid sorbent required to achieve such annual capture targets could be significant. Apart from the scale of material required to capture CO₂ at these rates, another challenge relates to quantifying the commercial-scale cost-savings for any given change in material properties. A recent study presents criteria to rank solvent properties according to their impact on CO₂ capture cost reduction.³² Compared to the benchmark monoethanolamine (MEA), postcombustion capture using aminosilicone solvents is estimated to reduce the parasitic energy loss from 30% to 18% and associated added COE from 74% to 44%.²⁸ The current challenge for sorbents development is to lower costs by maximizing the CO₂ desorption rate constant and minimizing the CO₂ reaction enthalpy, this is illustrated in Figure 1. While kinetic properties of the CO₂ sorbent drive the fixed capital costs, the thermodynamics govern the regeneration (operating) energy costs.³³ Beyond the economics, a comprehensive life-cycle analysis approach to carbon capture materials selection would take into account the environmental impact associated with their extraction, manufacture, use, and disposal. Unfortunately, very little data are available on the water, energy, or material footprint of candidate carbon capture materials. Such data would help researchers identify sustainable and industrially feasible materials, or classes of materials, with good carbon capture performance.

Another key aspect of carbon capture material selection is the type of stationary CO₂ source and associated infrastructure. Every source releases CO₂ in a gas stream of characteristic chemical composition, temperature, and pressure.^{21b} For

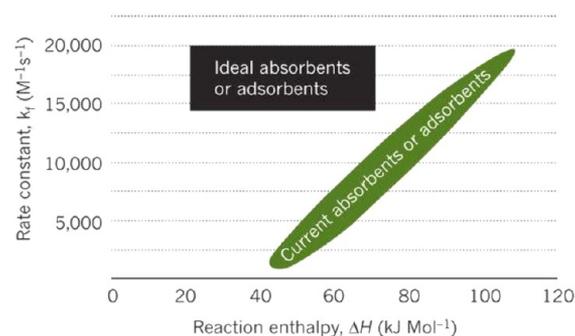


Figure 1. Kinetic vs thermodynamic material properties. Correlations between the rate constant and enthalpy of CO₂ sorption by current and ideal sorbent materials. Reprinted with permission from ref 33.

example, conventional fossil-fueled power plants produce a gas stream after combustion (postcombustion) composed of CO₂ in a majority of N₂ at atmospheric pressure. In addition, postcombustion capture imposes additional limitations on material properties associated with the process conditions and infrastructure already existing in place. If resources are available to move away from conventional infrastructures, alternative power plant designs may allow for more efficient carbon capture. For example, coal gasification plants produce a precombustion gas mixture composed of mostly CO₂ and H₂ at elevated pressure. In oxy-combustion, the resultant exhaust stream contains mainly H₂O and CO₂, which are very easy to separate. However, oxy-combustion requires high-purity O₂ as the oxidizing agent and thus O₂/N₂ separation is the challenge in this case. Because separation materials respond differently to each gas stream type and process condition, no single material is suitable for all scenarios. As illustrated in Figure 2, the CO₂ absorption capacity of chemical solvents is higher than that of physical solvents when separating CO₂ from a gas stream containing low CO₂ partial pressure.³⁴ In that light, each CO₂ source and associated capture infrastructure demands distinct materials property requirements, which have to be sufficiently characterized as noted previously and some of which can only be measured by diagnostic tools and methods commercially unavailable at present. Computational tools that allow material properties to be 'plugged-in' and optimized according to a given power plant model would be tremendously useful.

Solvents. In the solvent technology, CO₂ is removed via preferential dissolution of CO₂ over other gases present in the multicomponent gas stream. Depending on the gas stream characteristics, chemical or physical solvents can be used. Examples of chemical solvents are alkali carbonates, alkanolamines, and aqueous ammonia. Commonly used physical solvents include glycol ethers (Selexol) and methanol (Rectisol).^{21h,35} A list of commercial and noncommercial CO₂ scrubbing solvents can be found elsewhere.^{21h,29,36} Figure 3 shows a diagram of a typical postcombustion CO₂ capture technology using MEA.³⁷ In chemical absorption, the flue gas is cooled down and bubbled through the CO₂-lean solvent at temperatures between 40 and 60 °C, and CO₂ is absorbed. The CO₂-rich solvent is then pumped to the top of a vessel (desorber column) for regeneration with steam at elevated temperatures (100–140 °C) and close to atmospheric pressures.³⁸ For any set of process conditions, none of which are standardized, solvents are typically screened based on CO₂ capacity, rate of absorption, and heat of absorption. An ideal

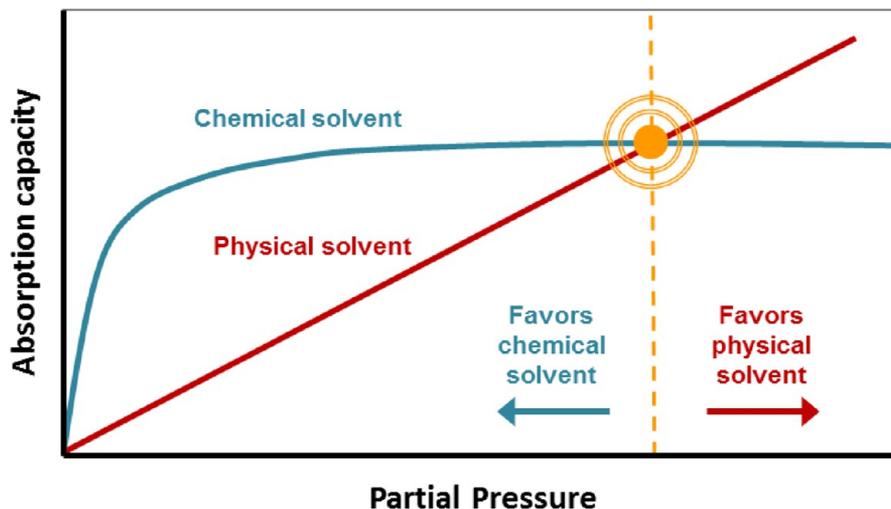


Figure 2. Comparison between physical and chemical solvents. Correlations between the rate constant and enthalpy of CO₂ sorption by current and ideal sorbent materials. Reprinted with permission from ref 34b.

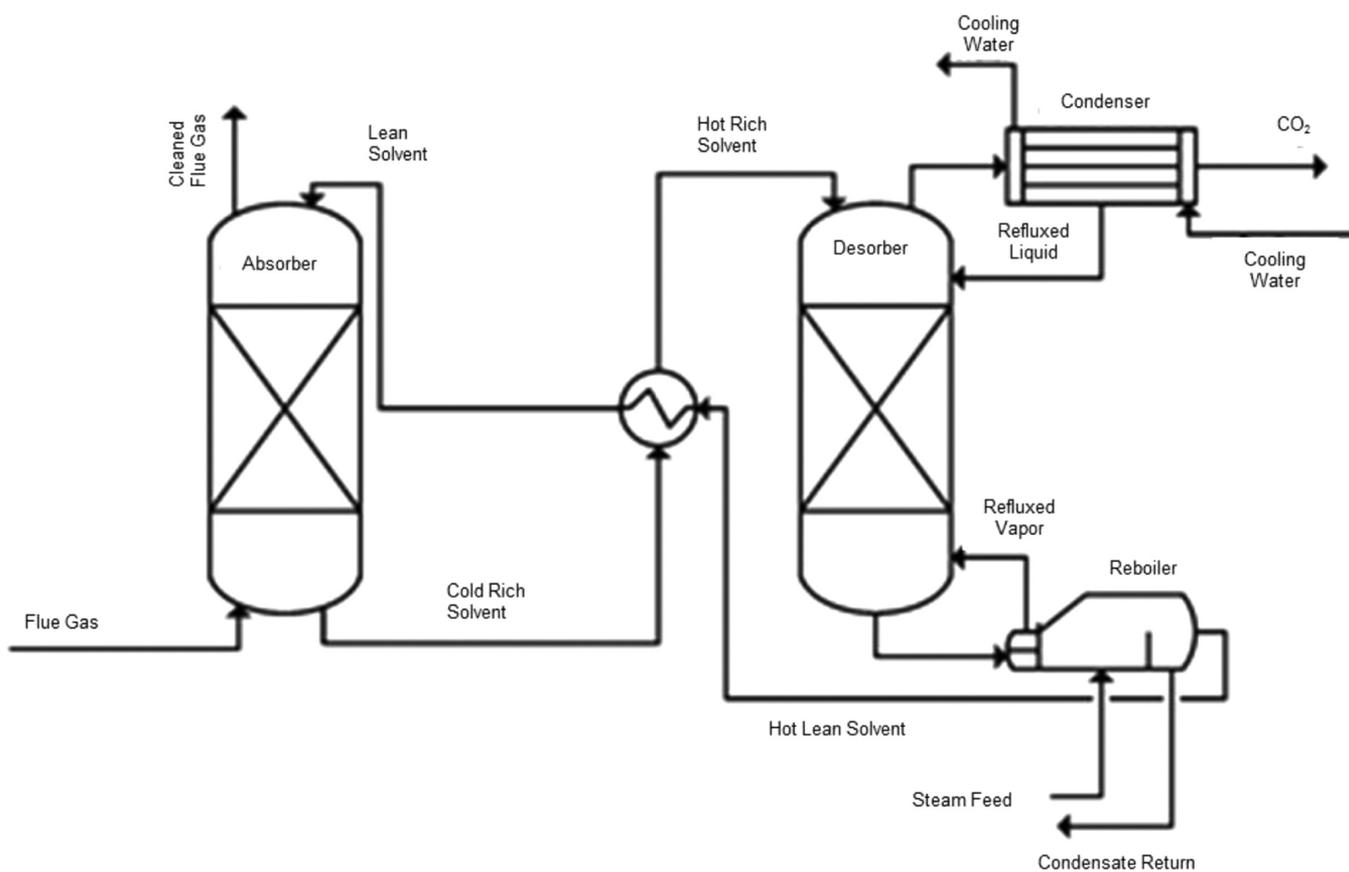


Figure 3. Solvent technology. Schematic of a basic chemical absorption process for amine based CO₂ capture. Adapted with permission from ref 37.

solvent would have a high CO₂ capacity to minimize solvent flow rate and heat requirement, a fast rate of CO₂ absorption to minimize the absorber size, and low heat of absorption to reduce energy use during regeneration.³² Other significant considerations include low toxicity, corrosiveness, and volatility as well as thermal and chemical stability.

Solid Sorbents. Gas separation using adsorbents is achieved via selective adsorption of a particular gas at the adsorbent’s surface or within its pore network. The major advantage of adsorbents over solvents is the absence of water,

which decreases regeneration energy requirements. Other benefits include low disposal/treatment costs and control of their microstructure and pore network to suit a particular function, for example molecular size sieving and multipollutant management.³⁹ Analogous to solvents, chemisorbents (chemically adsorb CO₂) are better suited to remove CO₂ from gas streams containing low partial pressure of CO₂ whereas physisorbents (physically adsorb CO₂ via, for example, van der Waals forces) are more appropriate for high CO₂ partial pressures.⁴⁰

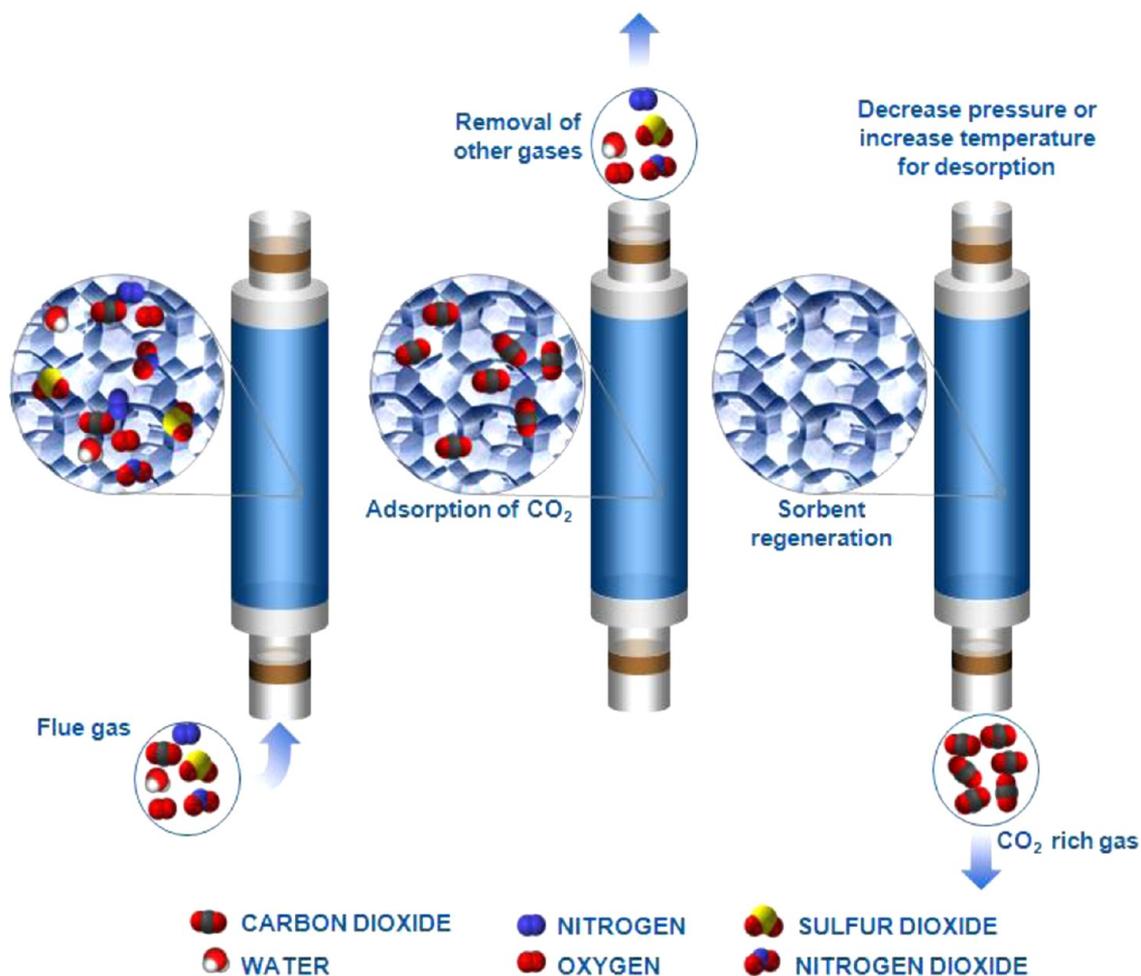


Figure 4. Solid sorbent technology. Schematic representation of a stationary (or fixed bed) sorption unit using solid sorbents for CO₂ removal from flue gas. Adapted with permission from ref 21b.

The most prevalent porous solids for removing CO₂ from natural gas, coal bed methane, and H₂-rich streams are aluminosilicate zeolite molecular sieves, titanosilicate molecular sieves, and activated carbons.^{21h} Other candidates include organic crystals, metal–organic frameworks, zeolitic imidazolate frameworks, and porous silicas or polymers functionalized with amine groups.^{21a,b,36a,40} While the CO₂ capacity of activated carbons and zeolites decreases with temperature, high temperature reactive solids that cycle between oxide and carbonate (e.g., CaO to CaCO₃, hydrotalcites, and LiZrO₃ to LiCO₃ and ZrO₂)^{21b,40} perform better at the high temperatures required for steam methane reforming and water gas shift reaction (e.g., 300–500 °C).^{21h} Overall, innovative adsorbents and process cycles remain in the R&D stage.^{12,29}

The process of adsorption can be performed in fixed sorption columns packed with solid sorbent particles or pellets⁴¹ or fluidized bed reactors.⁴² In moving bed reactors, the sorbent is transported cyclically between the adsorber and regenerator vessels, which adds mechanical property requirements. Figure 4 illustrates a typical stationary sorption reactor for CO₂ removal from flue gas. Depending on the properties of the sorbent, the sorption column can operate via pressure swing adsorption (PSA), temperature swing adsorption (TSA), or both. In PSA, gas adsorption occurs at increased pressure and desorption is triggered by lowering the pressure. Operating pressures are between 6 bar (0.6 MPa) for adsorption and 1.5 bar (0.15

MPa) for desorption at temperatures around 40 °C. However, higher pressures are used for removing CO₂ from certain H₂-rich gas streams.^{21h,43} In TSA, gas adsorption is done at atmospheric pressure and desorption is triggered by increasing temperature. Recent sorbent screening studies for postcombustion carbon capture report adsorption temperatures ranging between 55 and 60 °C and desorption temperatures between 55 and 150 °C.³⁹ For any given TSA, PSA, or hybrid TSA/PSA process, the performance of adsorbents is based on properties such as CO₂ capacity, sorption rate, heat of sorption, regenerability, and stability.²⁹ Solid sorbents with high CO₂ capacity and regenerability are attractive for minimizing the material footprint, reactor size, and thus capital cost. High selectivity toward CO₂ is also desired to increase the purity of the CO₂ recovered. Also, as indicated earlier in Figure 1, adsorbents with moderate heat of adsorption minimize regeneration energy requirements typically associated with conventional alkanolamine-based solvents, which have CO₂ bonding energies of the order of 100 kJ/mol.⁴⁴

Membranes. The separation of a gas from a multi-component combustion or industrial gas stream can be achieved using porous or dense membranes due to differences in the permeation properties between adsorptives. Membranes can be porous or dense. While porous membranes separate gases via differences in gas diffusion, dense membranes perform gas separation via differences in reactivities. Porous membranes

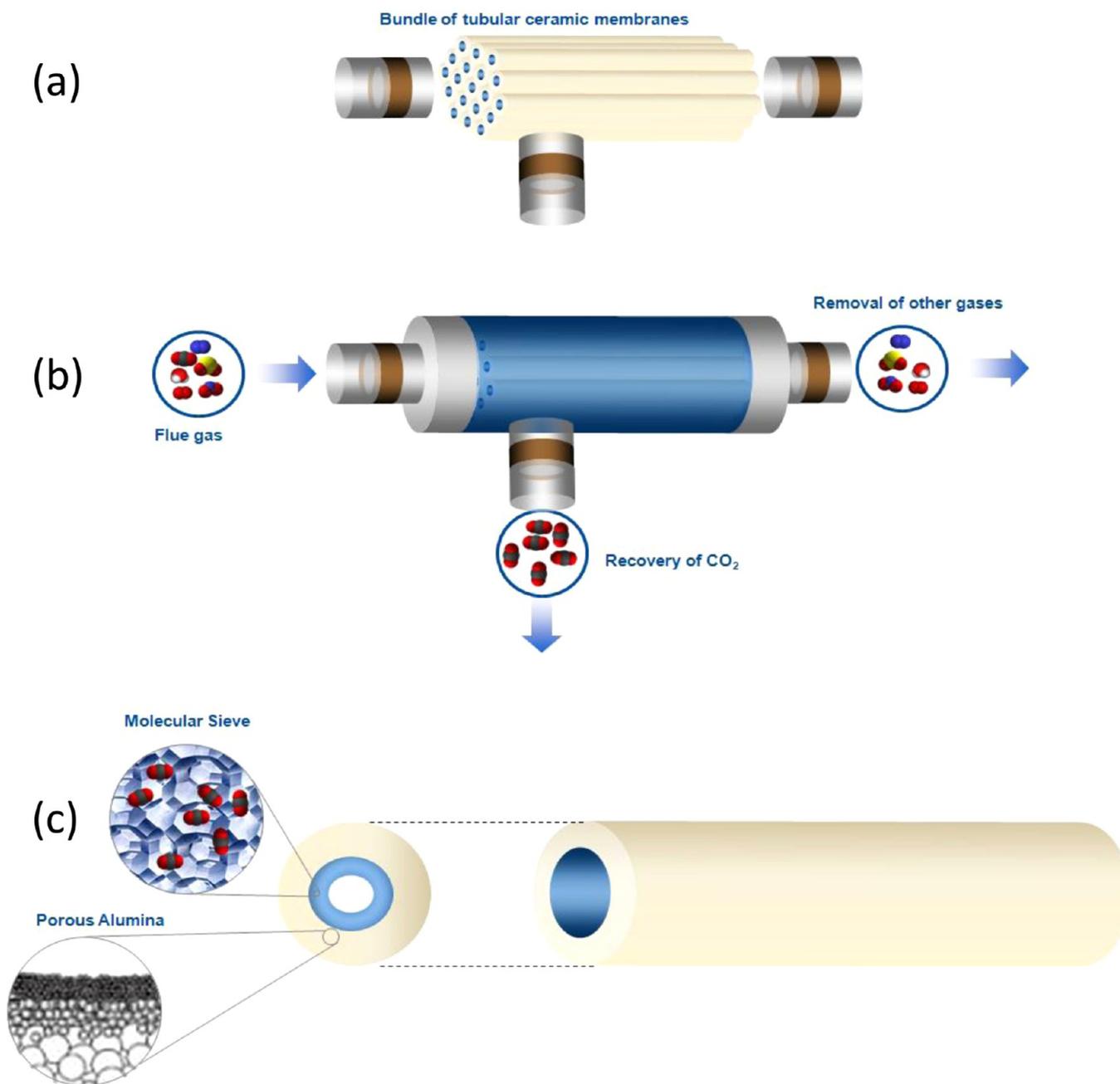


Figure 5. Membrane technology. Schematic diagram of the membrane technology featuring a ceramic-based porous support coated with an example molecular sieve material for removing CO₂ from flue gas: (a) bundle of ceramic based tubular membranes, (b) CO₂ separation column composed of a bundle of tubular membranes, and (c) close-up of a ceramic-based membrane. Adapted with permission from ref 21b.

are composed of a porous structural support and a thin functional layer material. In membranes containing pore between 0.5 and 20 nm, gas molecules permeate via convective flow with no selectivity. In membranes containing pores smaller than 0.5 nm, molecular size sieving can occur effectively. However, the manufacture of ultrathin molecular size sieving membranes at large-scale is difficult. In dense membranes, gas separation can be achieved by a solution-diffusion transport mechanism in which gas molecules first dissolve into or react with one phase of the membrane and then diffuse across the thickness of the membrane. Solution-diffusion transport membranes contain nondiscrete large pores filled with an absorption fluid such as ionic liquid.⁴⁵

Membrane technology offers numerous advantages over solvents and solid sorbents, such as absence of a regeneration step, small footprint, low capital investment, no moving parts, ease of installation, low environmental impact, ease of scaling up, and ease of testing new membrane products as materials innovation emerge.⁴⁶ While alkanolamine solvents generally dominate the natural gas purification market, membranes are preferred over solvents in cases where the natural gas contains high levels of CO₂. Nonetheless, membranes for the specific purpose of CO₂ recovery are a recent consideration. Numerous membrane configurations and candidate materials for carbon capture are being investigated.^{21c,29} Depending on the CO₂ source, intended separation mechanism, thermo-mechanical

stability requirements, and capital and operating cost targets, membranes can be made of different materials such as polymers (glassy or rubbery), metals, ceramics, or some combination of these. While polymeric membranes are inexpensive to fabricate on a large scale, inorganic materials offer better thermal stability and higher resistance to pressures, fouling, and chemically aggressive gas streams. A representative example of a layered porous membrane is shown in Figure 5, which features a ceramic-based porous support coated with a molecular sieve material (e.g., zeolite) for removing CO₂ from flue gas. When the flue gas enters the membrane vessel, a pressure differential across the membrane selectively forces a CO₂-rich gas to pass through. The residue, or retentate gas stream, that does not penetrate the membrane exits the vessel at the other end.²⁹

Key properties for screening carbon capture membrane materials include permeability, permeance, and selectivity, which determine the CO₂ recovery rate across the membrane and the purity of the recovered CO₂. In porous membranes, these properties are governed by the pore geometry and dimensions⁴⁷ and chemistry of the pore walls or material filling the pore. Analogous to the case of solid sorbents, economic analyses is essential for selecting membranes based on target properties for a particular CO₂ capture process. The most common low temperature membranes are made of polymeric supports functionalized with any of the following: zeolites, enzyme solutions, enzyme-synthetic analogues for facilitated transport, ILs, or another polymer.^{21c,h,48} Glassy polymeric materials such as cellulose acetate, polyimides, and polyaramides are commonly used for removing CO₂ from natural gas at the commercial scale. In membranes, the gas selectivity or separation factor generally decreases with increasing permeability of the more permeable gas in the mixture. For example, membranes made of rubbery polymers show CO₂/N₂ and CO₂/CH₄ selectivities of the order 40–60, much higher than that for glassy polymers. In contrast, rubbery polymers suffer from modest permeabilities due to their large degree of crystallinity.^{21h} The trade-off between selectivity and permeability has led to the development of empirical logarithmic relationships for important gas pairs (e.g., CO₂/CH₄) with upper bound limits that serve as a criteria to improve performance.⁴⁹

RESEARCH GAPS AND ACTIVITIES IN MEASUREMENT STANDARDS

Solvents. CO₂ Sorption. The design and optimization of gas treatment plants based on liquid chemical absorbers requires knowledge of fundamental physical, thermal, and transport properties of the gases and liquids involved in the process.^{22a} Among the most relevant data for optimizing a solvent-based CO₂ extraction process are CO₂ solubility (or capacity) and sorption rate.⁵⁰ CO₂ solubility, which can be obtained from vapor–liquid equilibrium (VLE) measurements, is defined as the relationship between the concentration of the gas in the solvent and its partial pressure in the gas phase at equilibrium. Once CO₂ solubilities at absorption and desorption conditions are known, several thermodynamic properties can be calculated, such as Henry's Law constants, activity coefficients, and enthalpies and entropies of absorption. In amine solutions, the CO₂ solubility depends on the partial pressure of CO₂ in the gas stream, operating temperature, type of amine, amine concentration in the solution, and the nature and concentration of other components in the amine solution, for example, O₂ and H₂S.

Given the wide range of parameters affecting CO₂ solubility, the amount of data required to cover all possible combinations and solvents in a database is enormous.^{22a,51} A number of VLE studies have been reported;^{51,52} however, there are significant gaps in solubility data at temperatures and pressures suitable for cost-efficient carbon capture. Such data gaps get larger because proprietary solvent formulations continue to emerge. The need for a comprehensive thermodynamic model to calculate CO₂ solubility in amine solutions has been recently reported in the context of carbon capture.⁵⁰ Discrepancies in data generated through available CO₂ solubility measurement methods⁵¹ call for the establishment of reliable experimental and computational measurements for CO₂ solubility.⁵³

Sorption Mechanism. Knowledge of the interactions between the functional groups in a particular solvent and CO₂ is essential for designing improved solvents based on structure–property relationships. In the case of amine-based solvents, the charge, size, charge dispersion, degree of solvation by water molecules, and intramolecular hydrogen bonds in the solvent play a role in the CO₂ sorption mechanism.^{52c} Thus, solvent molecular designs can be fine-tuned to target certain properties. As an example, the stability, CO₂ absorption capacity and enthalpy can be controlled by varying the weak proton donors in ILs containing a phosphonium hydroxide derivative.⁵⁴ Identification and quantification of the active species in a CO₂/solvent system is also key for determining the reaction mechanism and assessing the impact of a particular set of conditions on the interactions with CO₂. Advances in experimental equipment are needed to reveal the active molecular structures in a CO₂/solvent system at the intended absorption and regeneration conditions. Experimental data can be further complemented with computationally derived data to enable the visualization of molecular structures and design of enhanced performance solvents. While screening materials with high-throughput experimental methods is increasingly popular,^{50,55} design of new molecules with better performance could be accelerated with the development of predictive computational tools⁵⁶ that make use of experimental correlations.⁵⁷

Corrosion and Degradation. Aqueous amine-based solutions are prone to oxidative degradation in the presence of flue gas O₂ and other oxidizing agents,⁵⁸ which challenges the use of these materials for carbon capture.⁵⁹ Oxidative degradation can lead to frequent solvent replacement to maintain CO₂ absorption capacity and increases the amount of waste products, which may impact environmental and human health.⁵⁹ In addition, the oxygen present in flue gas and byproducts of amine degradation can corrode the metal infrastructure.⁶⁰ Dissolved CO₂ has also been reported to be a primary corroding agent in alkanolamine gas treating plants, with the following order of corrosiveness to carbon steel: primary amines > secondary amine > tertiary amines.⁶¹ As mentioned earlier, degradation and corrosion issues also increase CO₂ capture costs.⁶² Although removing O₂ from flue gas prior to CO₂ capture would help avoid this problem, that approach would also increase process costs. An alternative solution relies on the use of corrosion inhibitors,⁶³ developed by the chemicals industry to protect metal components in direct contact with oxygen, amine solutions, and its degradation products.⁶⁴ Optimizing corrosion inhibitors for improving the performance of amine solvents is hindered by a lack of sufficient relevant data in the open literature. In order to advance the design of corrosion inhibitors and improve amine-based solvent performance, reliable analytical methods are

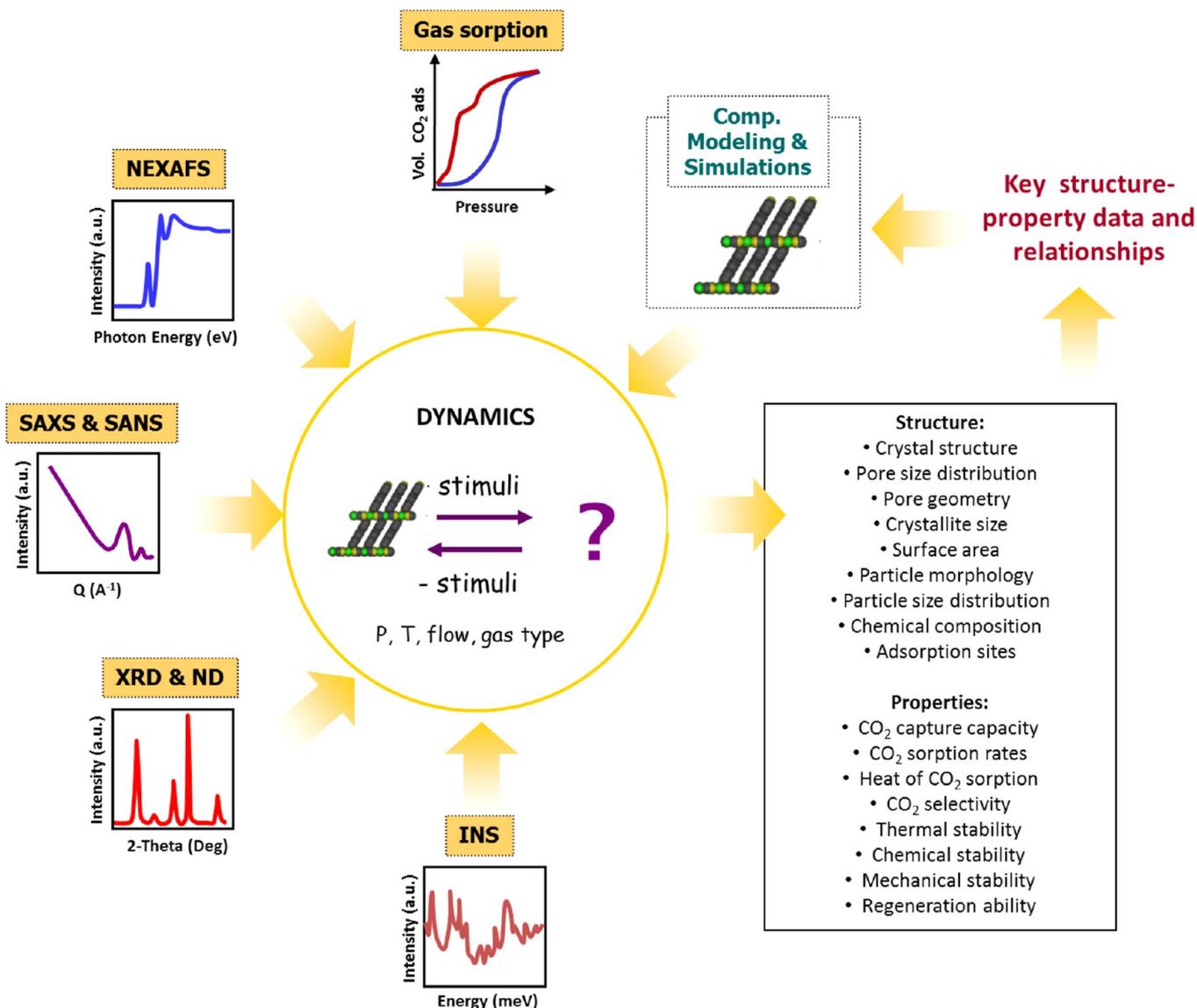


Figure 6. Summary of NIST activities in support of carbon capture materials development. Suite of experimental and computational measurement tools to study the CO₂ capture mechanism and characterize the structural response of crystalline solid sorbent materials upon exposure to various gas stream types at different temperature and pressure conditions. The acronyms shown in the labels are defined as follow. NEXAFS: near edge Xray absorption fine structure, SAXS: small angle X-ray scattering, SANS: small angle neutron scattering, XRD: X-ray diffraction, ND: neutron diffraction, INS: inelastic neutron diffraction.

needed for determining the type and amount of degradation products and accurately quantifying the maximum levels of oxygen and degradation species that common metal infrastructure components can withstand before corroding.

Solid Sorbents. CO₂ Sorption. The design of commercial CO₂ capture units using adsorbents for various process equipment options requires lab-scale screening of materials based on basic performance indicators. As pointed out elsewhere,^{40,65} suitable sorbent selection criteria must consider all of the relevant sorption properties. However, target specifications for CO₂ sorption materials, for example, working capacity, selectivity, sorption rates, enthalpies of sorption, heat capacity, attrition resistance, stability to acid gases, have not been established. In particular, heat capacity is a property rarely reported for solid sorbents despite it being an essential thermodynamic quantity required to calculate regeneration energy. The lack of international consensus on lab-scale sorbent

performance metrics and recommended conditions for testing sorbents leads to gaps in available data and a limitation for in-silico material discovery. Current screening studies must rely on computationally derived CO₂ sorption data to fill experimental data gaps.⁶⁵ Even if only partially available, experimental data could be used to validate and select the most suitable atomic force fields for calculating the sorption properties of some materials. We note that establishing an ideal array of performance metrics is not trivial as each sorbent family will require a different combination of property targets in order to achieve the same cost savings for each CO₂ capture process.

When establishing sorbent performance metrics, lab-scale evaluation of the thermal and chemical stability of adsorbents in the presence of representative gas impurities and moisture levels should be considered. However, such measurements are only currently accessible at the pilot-plant level.⁶⁶ In addition, although commercial lab-scale equipment is readily available to

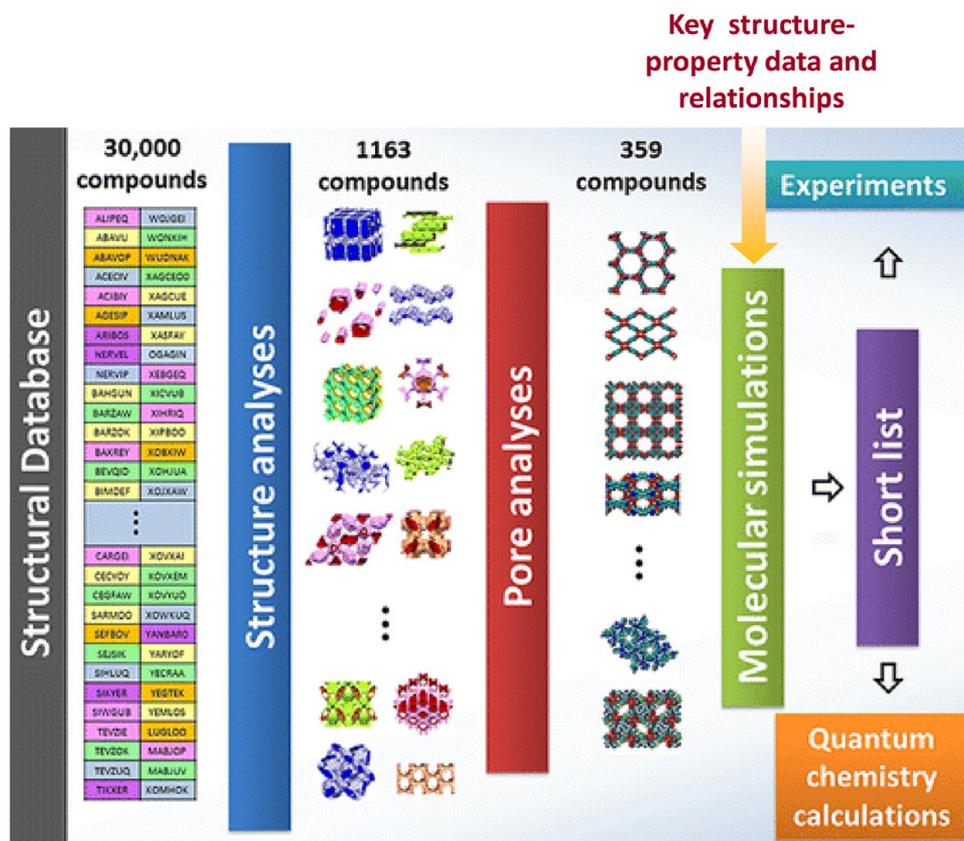


Figure 7. Computational tool for selecting carbon capture materials. . Example of a computational tool to select promising membrane materials for CO₂/N₂ separation within the family of Metal-Organic Frameworks. The figure highlights the potential role of key structure-property relationships in the workflow for material screening. Adapted with permission from ref 82. Copyright 2012 American Chemical Society.

measure sorption properties over a wide range of pressures and temperatures, recommended sorbent evaluation protocols have yet to be established. Consequently, performance data for CO₂ capture materials continues to be reported over a wide range of conditions. For example, two separate sorbent screening studies for CO₂ separation from flue gas assumed different CO₂:N₂ ratios.^{65,67} Further, despite the importance of evaluating competitive gas sorption properties of adsorbents, several technological challenges still exist for reliably measuring multicomponent gas sorption isotherms.⁶⁸

A recent interlaboratory study shows that supercritical CO₂ sorption on a well-characterized activated carbon sample can be determined accurately with both gravimetric and manometric instruments but requires thorough equipment optimization and proper sample preparation procedures.⁶⁹ In addition, calibrating equipment, and comparing the performance of sorbents across laboratories worldwide cannot be done without SRMs. Having an international consensus on the equipment characteristics, operating parameters, and real gas laws (or equations of state) to be used for measuring the CO₂ sorption properties of a model material (i.e., a material that is well characterized and its structure and properties are understood), would greatly impact the carbon capture community. Such measurement protocols are needed not only for high pressure sorption of CO₂ but also for CO₂ gas mixtures and other gases as well.^{68b} NIST researchers with support from the U.S. Department of Energy's Advanced Research Projects Agency-Energy (ARPA-E) are building a state-of-the-art Facility for Adsorbent Characterization and Testing (FACT). FACT will serve the sorbent materials research community by providing impartial testing

and characterization of material sorption properties, establishing reference materials and testing procedures, and disseminating sorbent material property data and measurement "best practices".

Sorption Mechanism. Correlating enhanced CO₂ capture behavior to changes in specific physicochemical characteristics of a sorbent material is very valuable for facilitating the development and optimization of solid sorbents. A recent evaluation of a specific set of candidate postcombustion capture materials reports that CO₂ selectivity is a function of the heat of CO₂ adsorption and is not necessarily related to surface area and pore size.⁶⁷ Conversely, in molecular sieve materials such as manganese oxide, the larger affinity toward CO₂ over N₂ has been partially attributed to the pore size.⁷⁰ Typically, structure–property relationships are derived from data obtained from ex-situ structure determination methods, that is, before or after the sample has been subjected to the adsorption event. However, there is a need for developing experimental and computational tools for characterizing CO₂/sorbent systems in situ. For example, it is known that CO₂ selectivity in mesoporous silica and some metal–organic frameworks can be enhanced through the incorporation of amine functionalities.^{40,71} The performance of such materials critically depends on the accessibility of the CO₂ molecules to the amine moieties under the intended operating conditions, which would contribute to the compilation of structure–property correlations for a given class of materials in their actual 'active' state.⁴⁵ The use of in situ techniques spanning a wide range of length scales can help unravel the sorption mechanism of a material as a function of operating conditions in real time.

NIST researchers are developing sorbent property diagnostic tools and computational platforms for gas sorption mechanism determination (Figure 6). In collaboration with the University of Connecticut, NIST scientists established a combined experimental/computational method for understanding the mechanism driving the hysteretic CO₂ sorption and preferential adsorption of CO₂ over N₂ in molecular sieves with manganese oxide framework.⁷⁰ NIST researchers are also developing an efficient method for simulating gas adsorption processes based on grand canonical transition-matrix Monte Carlo,⁷² of particular relevance for subcritical gas adsorption in which capillary phase transitions occur. Further, research at NIST involves the development of advanced in situ characterization methods based on X-ray and neutron scattering as well as spectroscopic techniques.⁷³ In a collaborative study, scientists from NIST and NETL demonstrated the use of in situ small angle neutron scattering (SANS), in combination with other analytical tools developed at NETL, for confirming the dynamic pore-opening factor that governs CO₂/N₂ selectivity in a specific flexible metal organic framework.⁷⁴ In addition, NIST and Georgia Tech researchers have jointly explored the use of near edge X-ray absorption fine structure (NEXAFS) spectroscopy, on a synchrotron beamline equipped with a gas dosing chamber, to probe the surface state of an amino-functionalized mesoporous silica after immediate exposure to CO₂.⁷⁵ Apart from in situ characterization techniques that are only available at synchrotron X-ray and neutron user facilities, NIST scientists have also begun to test lab-scale in situ structure determination methods. A prototype high pressure environmental cell with automated gas delivery is currently being tested for the development of lab-scale powder XRD measurements to determine crystal structures in situ.

Experimental and modeling advances at NIST will provide sorbent developers with suitable tools for extracting reliable structure–property correlations, which are valuable for in-silico screening and design of improved materials. An example of in-silico screening of metal organic frameworks for CO₂ separation is illustrated in Figure 7. Although this example features metal organic framework (MOF) membrane materials, NIST's role would also extend to solid sorbents. In this example, NIST's role could involve the generation of another sorbent screening criteria based on structure–property relationships derived from in situ characterization techniques in which materials display structural features only available in their “active” state. Advances in experimental and computational methods to determine gas sorption mechanisms at NIST can be used to validate and improve computational models and further enhance predictive molecular simulations tools.

Pore Size Distribution. An important attribute of porous solids is specific surface area, which can range from a few hundred m²/g to over 3000 m²/g. Large surface areas, which enable large amount of adsorbed gas, can be achieved through either small particles or highly porous internal structures.⁴⁵ Porous solids must also have large pore volumes with pore sizes big enough to allow the target CO₂ molecules to enter,^{36c,65} which have a kinetic diameter of approximately 3.30 Å (0.33 nm).⁷⁶ Currently, the determination of micro- and meso-pore size distribution by commercial equipment relies on a limited selection of force fields only developed for silica and carbon chemistries with the following pore geometries: slit-shape, cylindrical, and spherical. Given the wide range of CO₂ capture materials that have emerged in recent years, suitable force fields

are needed to cover a larger number of chemistries and complex pore networks.

Membranes. CO₂ Separation. Similar to the case of sorbents, an array of target values for lab-based membrane performance indicators such as permeability, permeance, and selectivity according to each relevant gas stream has not been established. Such information can be obtained from rigorous cost analyses, which are not available in the open literature. The subcommittee of the Chemical Industry Vision 2020 Technology Partnership on Carbon Dioxide Separation Technology^{21h} recently reported as one of its near term goals the development of polymeric membranes with a CO₂/H₂ selectivity between 15 and 20 (or higher), with double the CO₂ flux of current commercial membranes and stability to temperatures higher than 200 °C. Although providing very useful information, neither the methodology used to arrive at those recommended values nor the cost savings associated with each of the property improvements was described. Scientists need better understanding of the cost benefit of improving a certain property as well as agreement on the exact temperature, pressure, gas composition, and moisture content conditions at which target properties should be achieved. A case in point is the setting of the permeate pressure for membrane testing at atmospheric pressures, which has led to the use of permeate pressures sometimes 15.5 kPa apart depending on the geographical locations where experiments are performed.⁷⁷ A consensus on suitable operating conditions for membrane performance testing and specific model CO₂ capture cases would avoid the publication of mismatched data and further facilitate computational-aided screening of materials.

Transport Mechanism. Understanding the complex mechanism of CO₂ transport through a membrane is crucial for achieving the right balance between permeability and selectivity. In porous membranes, gas/solid interactions play an important role in the transport of molecules apart from molecular size and shape. For example, the permeance of CO₂ in a zeolite-based membrane has been reported to be larger than that of H₂ even though the kinetic diameter of H₂ is smaller than that of CO₂.⁷⁸ Overall, the CO₂ permeability is a function of CO₂ sorption properties and diffusion mechanisms, although most of the effects of confinement on gas diffusion are not well understood. Gaining knowledge on the physical and chemical factors governing confinement effects could particularly be relevant for ILs,⁷⁹ commonly embedded in porous supports to facilitate CO₂ transport. The use of ILs has attracted attention due in great part to the large number of possible cation/anion combinations available to adjust properties (e.g., imidazolium, pyridinium, ammonium or phosphonium cations, coupled with a large variety of possible anions), negligible vapor pressures, and stability to temperatures above 200 °C.^{48,80} However, little is known about the IL/CO₂ bonding mechanism, local structure, and ion dynamics responsible for the unique solvent properties. Advances in experimental equipment and associated computational platforms are needed to bring the CO₂ transport mechanisms of IL-membrane components to light at realistic operating conditions.

The development of nanocomposite membranes is increasing but requires advances in our ability to screen candidate membranes for permeability. CO₂ diffusivity measurements would enable faster estimations of the CO₂ permeability for membranes with known CO₂ sorption (or partition) coefficients. However, quantifying the effect of competing

Table 3. Selected Research Gaps and Examples of Potential Standards

examples of potential standards	TE ^a	EB ^b
solid sorbent or membrane reference materials with minimum acceptable CO ₂ sorption or transport properties for proper instrument calibration.	high	medium to high
measurement protocols for high pressure gas sorption experiments for single- and multicomponent gases.	high	high
standardization of the equations of state to be used by high pressure gas sorption instruments not only for CO ₂ but also for CO ₂ gas mixtures as well as other relevant gases.	low	high
establishment of the standard composition and total pressure of model gas mixtures that best represent each CO ₂ capture scenarios, i.e., flue gas, precombustion gas stream, natural gas.	medium	medium

^aTE: (difficulty of) technical effort. ^bEB: economic benefit.

gases on diffusion coefficient calculations is a challenge.⁸¹ Similarly, high-throughput computational tools are needed to screen composite materials.⁸² An example of such an in-silico screening tool to down-select MOF membrane materials is presented in Figure 7. The continued development of hybrid experimental/computational methods to quantify CO₂/membrane material interactions, ion dynamics, and gas diffusion is needed to lead to the development of better membranes.

Microstructure and Interface. The multicomponent nature of recent nanocomposite membrane developments calls for the establishment of techniques to measure the spatial distribution of components and microstructure. For example, MOFs are incorporated into polymeric nanocomposites to enhance gas permeability without compromising selectivity.⁸³ In these membranes, a good dispersion of MOF particles throughout the matrix and strong interfacial interaction are desired to minimize the installation size and maintain performance. Overall, quantitative approaches are needed to measure tortuosity, pore filling, and dispersion at different stages of the membrane fabrication and under relevant operating conditions in order to draw structure–property correlations. The degree of pore filling by a functional material (ionic liquid, zeolite, or enzyme) depends on the type of porous support, the physical and chemical interactions between host and guest materials, and the procedure used for guest incorporation. Tortuosity reflects the length of the average pore of the membrane compared to the membrane thickness. Typical tortuosity values range between 1.5 and 2.5, as pores tend to meander rather than align perfectly as cylinders (i.e., tortuosity equal to one).⁸⁴ Such advances in measurement science would enable the optimization of membrane fabrication with tailored and stable microstructures, interfacial architectures, and tortuosity patterns.

Examples of Potential Standards for Carbon Capture.

To illustrate the expected benefits and costs associated with advancing measurement standards needed to support the innovation in carbon capture materials, a selected set of examples of research gaps are presented in Table 3. The examples are ranked in terms of their technical effort (TE) and economic benefit (EB). The rating levels assigned to either TE or EB were relative in value, that is, low, medium, or high. As shown in Table 3, a high TE is required for both the development of standard reference materials (SRMs) for CO₂ sorbents or membranes and the establishment of measurement protocols for high pressure gas sorption experiments for single- and multicomponent gases. SRM development in this field is very difficult because standardized measurement protocols are essentially not available. The difficulty of establishing measurement protocols lies on the multipoint nature of the measurements and the numerous sources of uncertainty, which includes sample activation procedures. Also, in some cases, a full scale interlaboratory study (ILS) is required to test the robustness of

the method, which demands a lot of time and effort. If these methodologies were standardized, the impact on the carbon capture materials community would be significant, which explains the EB assignment as high. Once measurement protocols are in place, the EB of SRM development would be from medium to high. Another example, listed in Table 3, involves the standardization or implementation of up-to-date real gas laws or equations of state by high pressure gas sorption instruments, which would require a low TE. The pressure-volume-temperature data are available but have not been built into the data analysis software by all instruments manufacturers. While the TE is considered low, the EB would be high because it significantly reduces uncertainty in the measurement and would make cross-laboratory comparisons more uniform. Finally, the last standard example listed relates to the establishment of the standard composition and total pressure of model gas mixtures, which is also very important. However, compared to the other standard examples, the development of model gases will require medium TE and the economic impact (EB) would also be medium.

CONCLUSIONS

The anticipation of possible national and international CO₂ emissions regulations has prompted the development of numerous carbon capture materials aimed to reduce the environmental impact of CO₂-emitting technologies. Several research gaps have been identified in the development of measurement standards, which limit the pace at which solvents, solid sorbents, and membranes can be optimized. The lack of an established battery of laboratory-based property targets for adsorbents and membranes in the context of the different carbon capture options continues to be a difficulty for optimizing both the equipment to measure key properties and the environmental benefits of these materials. NIST is playing an important role as an NMI in the field of carbon capture to support materials research and development. Reliable experimental and computational diagnostic tools are being developed to determine important CO₂ sorption properties and reaction mechanisms in selected model solid sorbent materials and in situ facilities and lab-scale instrumentation are being established for the determination of the physical and chemical characteristics of adsorbents in their 'active' state. The new ARPA-E-sponsored adsorption facility being built at NIST will provide the sorption community with the right set of measurement tools and measurement methods to accelerate adsorbent materials innovation. The continuous advancement in measurement science, protocols, and standards targeted to carbon capture materials is essential if emerging materials are to meet the challenges of new technologies, the risks of changing requirements, and opportunities of potential markets that are ahead.

■ ASSOCIATED CONTENT

5 Supporting Information

A carbon capture primer is provided in the Supporting Information to describe the different carbon capture options including include postcombustion, precombustion, oxy-combustion, and capture from other industrial process streams (Figures S1–S3). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

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- (86) 77 FR 41051 Prevention of Significant Deterioration and Title V Greenhouse Gas Tailoring Rule Step 3 and GHG Plantwide Applicability Limits; Final Rule.
- (87) 74 FR 56260 Mandatory Reporting of Greenhouse Gases; Final Rule.
- (88) (a) Monitoring of GHG data began in 2010 and the first reports were submitted to EPA in September 2011. Data are now

available for 2010 and 2011, see Ref. V. Additional rulemakings have been released since 2009 to modify the program as needed, see Ref. W.

(b) Greenhouse Gas (GHG) Data; <http://www.epa.gov/ghgreporting/ghgdata/index.html>; (c) Rulemaking Notices; <http://www.epa.gov/ghgreporting/reporters/notices/index.html>

(89) 75 FR 77230 Federal Requirements Under the Underground Injection Control (UIC) Program for Carbon Dioxide (CO₂) Geologic Sequestration (GS) Wells; Final Rule.

(90) 76 FR 56982 Announcement of Federal Underground Injection Control (UIC) Class VI Program for Carbon Dioxide (CO₂) Geologic Sequestration (GS) Wells.