



## Materials challenges in carbon-mitigation technologies

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Given the increasing size of CO<sub>2</sub>-generating industries and the mounting awareness of their environmental impact, carbon-management technologies are expected to play an important role in curtailing environmental emissions in coming years. A major challenge in carbon management is the development of cost-effective, technologically compatible, and efficient CO<sub>2</sub> capture and storage technologies. The development of energy-efficient solvent, solid-sorbent, and membrane materials to capture CO<sub>2</sub> from industrial exhaust streams can take improvements in process efficiency one step further. Also, the permanent storage of CO<sub>2</sub> in geologic formations is critical to the success of carbon-management technologies and requires better understanding of interactions of CO<sub>2</sub> with underground materials. These and other materials challenges must be solved to make carbon capture and storage an economically viable and reliable technology to be adopted by the power and product manufacturing industries.

### Introduction

Reducing greenhouse gas emissions from the power generation and industrial sectors is an important component of environmental sustainability. The large volume of CO<sub>2</sub> emissions from these point sources and their stationary nature makes them particularly attractive targets. The complex global challenge is to reduce CO<sub>2</sub> emissions while simultaneously generating energy, products, services, buildings, and public infrastructure for the continuously rising population worldwide, estimated to surpass nine billion by 2050.<sup>1</sup>

Global efforts to stabilize the atmospheric CO<sub>2</sub> concentration require continual advances in carbon-mitigation technologies to reduce carbon sources and increase carbon sinks. Approaches to reduce carbon sources include increasing the efficiency of energy conversion and utilization; improving building insulation for energy conservation; and adopting more alternative, non-carbon energy sources such as nuclear energy and renewable fuels. In addition, natural carbon sinks, such as forests and soils, can be expanded to enhance their CO<sub>2</sub>-absorption capacities, and artificial carbon sinks can be engineered in oceans and underground geological formations for long-term storage of CO<sub>2</sub> through a process called carbon sequestration.<sup>2</sup>

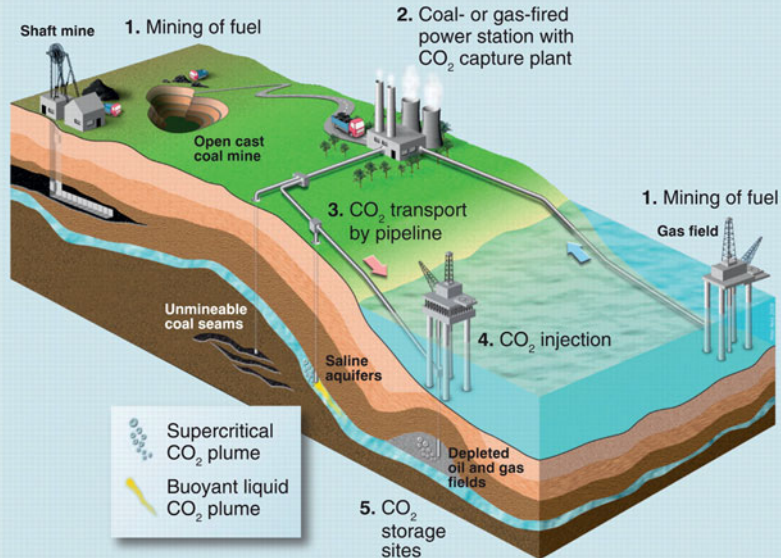
The life cycle for a fossil fuel, including proposed carbon capture and storage (CCS) in underground geological formations, is illustrated in **Figure 1**. The fossil fuel extracted during mining (step 1) is used for power generation by a

thermochemical conversion process, which produces CO<sub>2</sub> emissions. The exciting mitigation opportunities for a materials scientist begin at the smokestack (step 2), where significant advances in solvent, solid-sorbent, and membrane materials are needed to cost-efficiently capture significant amounts of CO<sub>2</sub> before it spreads into the atmosphere. Once the CO<sub>2</sub> is captured, the role of a materials scientist continues downstream. For example, low-cost corrosion-resistant pipelines are needed to transport CO<sub>2</sub> (step 3) to a suitable site for injection (step 4) and storage (step 5) underground, where the interactions between fluids (e.g., CO<sub>2</sub>, water, oil) and natural and engineered materials (e.g., minerals, cement, steel) are very important. In the present article, we survey research opportunities for materials scientists in the development of carbon-mitigation technologies for energy and other industrial sectors. We emphasize storage of captured carbon in underground geological formations, which can lower emissions from large, stationary, point sources.

### Carbon dioxide sources and flue-gas types

A “large” source is defined as one that emits more than 0.1 Mt of CO<sub>2</sub> per year. Approximately 8000 large CO<sub>2</sub> sources have been identified worldwide, including coal-fired power plants, oil refineries, and cement manufacturers, together emitting 18 Gt of CO<sub>2</sub> per year.<sup>2,4</sup> The purpose of CO<sub>2</sub> capture from a stationary or point source is to produce a stream of concentrated CO<sub>2</sub>

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**Figure 1.** Schematic representation of the life-cycle chain of a fossil fuel with carbon capture and storage into underground geological formations. (Reproduced with permission from Reference 3. © 2009, American Association for the Advancement of Science.)

that can be pressurized and transported to a suitable location for permanent storage. The extra cost depends on many details about the source, especially the partial pressure of CO<sub>2</sub>.

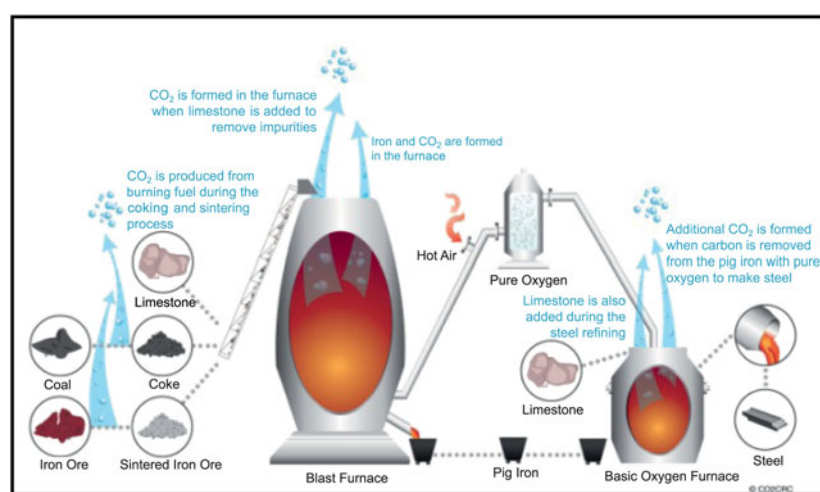
In conventional fossil-fuel combustion, the primary fuel is burned in air to produce heat, which generates steam and power. The effluent, referred to as “flue gas,” typically has a CO<sub>2</sub> concentration on the order of 15 vol% for air-fired, coal-based processes.<sup>2</sup> The temperature and pressure of the flue gas depend on process conditions including feedstock, oxidant, and gas-processing steps, but are typically ~65°C and ~2 bar, respectively. Such dilute, low-pressure streams of CO<sub>2</sub> present a challenge for cost-effective gas separation. Advanced energy-conversion technologies are under development to increase the energy-conversion efficiency and facilitate carbon capture. These include the use of coal with indigenous or carbon-neutral “opportunity fuels” such as biomass.<sup>5</sup>

Industrial processes employ similar fossil-fuel-based conversion technologies to meet process-related energy requirements and supply chemical feeds. **Figure 2** shows an example of an industrial source of CO<sub>2</sub>: iron and steel production. Depending on the specifics of the process, chemical reactions and material transformations might be deployed in combination with the combustion step, producing a flue gas distinct from that of power plants. For example, the extraction of metals from ores uses carbon as a

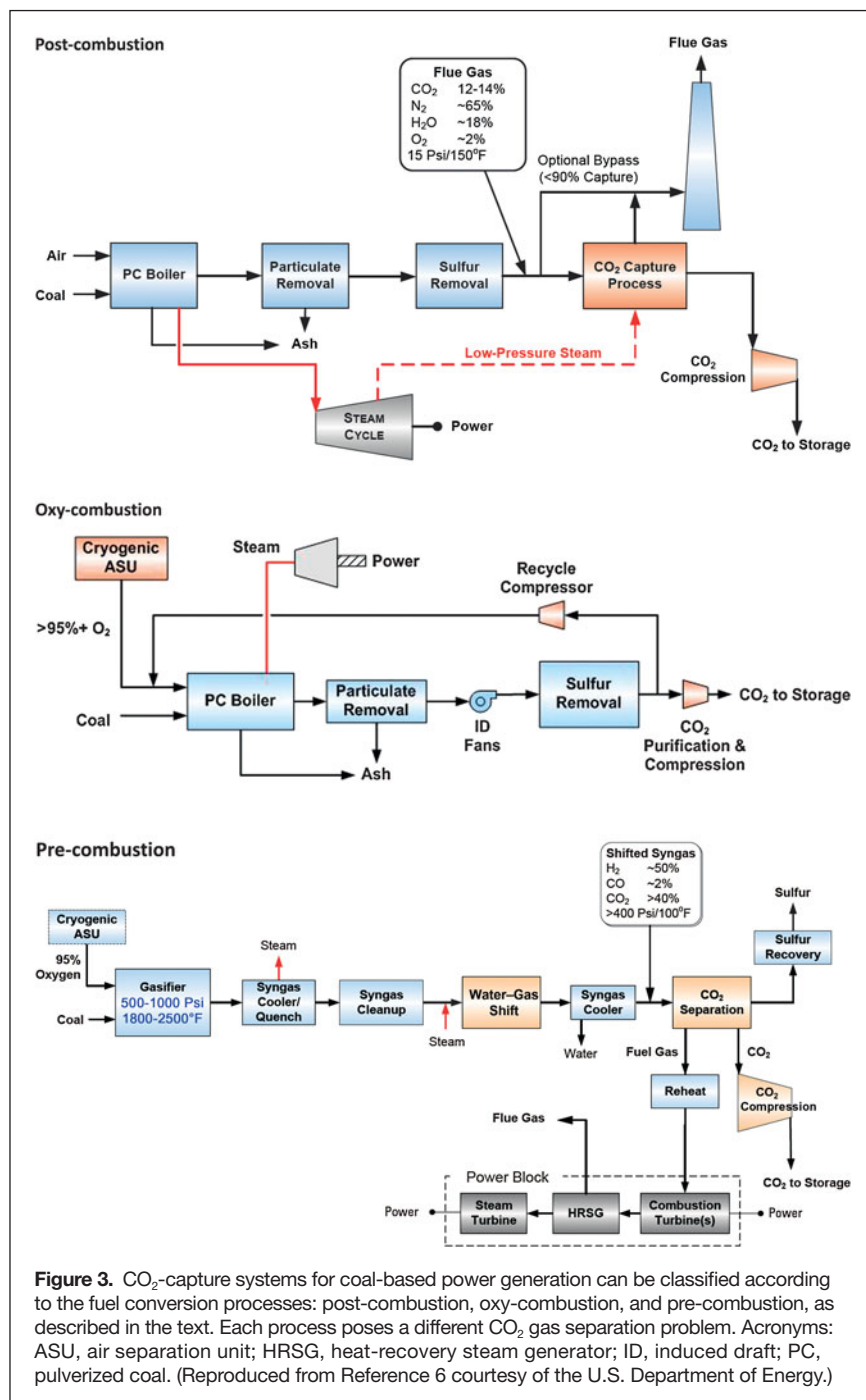
reducing agent and produces a flue gas with a CO<sub>2</sub> concentration between 15 vol% and 27 vol% and partial pressures between 0.3 bar and 0.6 bar.<sup>2,4</sup> Although fermentation, natural-gas processing, and gasification emit less than 2% of the CO<sub>2</sub> from large, stationary sources, their high CO<sub>2</sub> partial pressures make them promising for early deployment of CCS systems.<sup>2</sup>

### Carbon dioxide capture systems and technologies

The main approaches to CO<sub>2</sub> capture from power plants and industrial emissions are classified according to the fuel conversion process, as illustrated in **Figure 3**. *Post-combustion* refers to the separation of CO<sub>2</sub> from flue gas produced by conventional complete oxidation of the primary fuel—coal, natural gas, oil, or biomass—in air. *Oxy-combustion*, a technology that is still under development, instead uses high-purity O<sub>2</sub> as the oxidizing agent. This makes recovery of CO<sub>2</sub> easier, because the resultant flue gas is mainly H<sub>2</sub>O and CO<sub>2</sub>. *Pre-combustion* starts with the partial oxidation of the primary carbon fuel to produce synthesis gas, or “syngas,” composed of CO and H<sub>2</sub>. The carbon monoxide is further oxidized with steam in the catalyzed water–gas shift reaction to produce a mixture of hydrogen with CO<sub>2</sub>, which is then captured.<sup>2</sup> Each option poses a different gas-separation problem: CO<sub>2</sub> from N<sub>2</sub> at atmospheric pressure for post-combustion, O<sub>2</sub> from N<sub>2</sub> in air (or O<sub>2</sub> generation) for oxy-combustion, and CO<sub>2</sub> from H<sub>2</sub> at elevated pressure for pre-combustion.



**Figure 2.** Major sources of CO<sub>2</sub> include iron and steel production, shown here, as well as coal-fired power generation, cement manufacturing, and ammonia production, each emitting flue gas with distinct properties. (Image obtained from CO2CRC, Cooperative Research Centre for Greenhouse Gas Technologies, Canberra, Australia. © 2011, CO2CRC.)



where components of the gas mixture permeate through the membrane at different rates because of their physical and chemical interactions with the membrane. In *cryogenic* distillation, a gas mixture is liquefied through a series of compression, cooling, and expansion steps, and the gas components are separated by distillation.

The best currently available capture technology is based on chemical solvent absorption in a post-combustion system. This technology is expensive and energy-intensive, in great part because of the energy required to regenerate the capture material.<sup>7</sup> Incorporating such capture technology into a supercritical coal power plant is estimated to increase electricity cost by 70% relative to a similar plant without capture.<sup>8</sup> The major contributors are equipment and materials (~27% of the increase); capture-material regeneration (~44%); process pumping and compression (~6%); CO<sub>2</sub> compression (~13%); and CO<sub>2</sub> transport, storage, and monitoring (~9%).<sup>9</sup> Given the substantial costs associated with current technology, great opportunities exist for materials scientists to develop improved carbon-capture materials. The following sections describe the materials challenges for the different combustion systems.

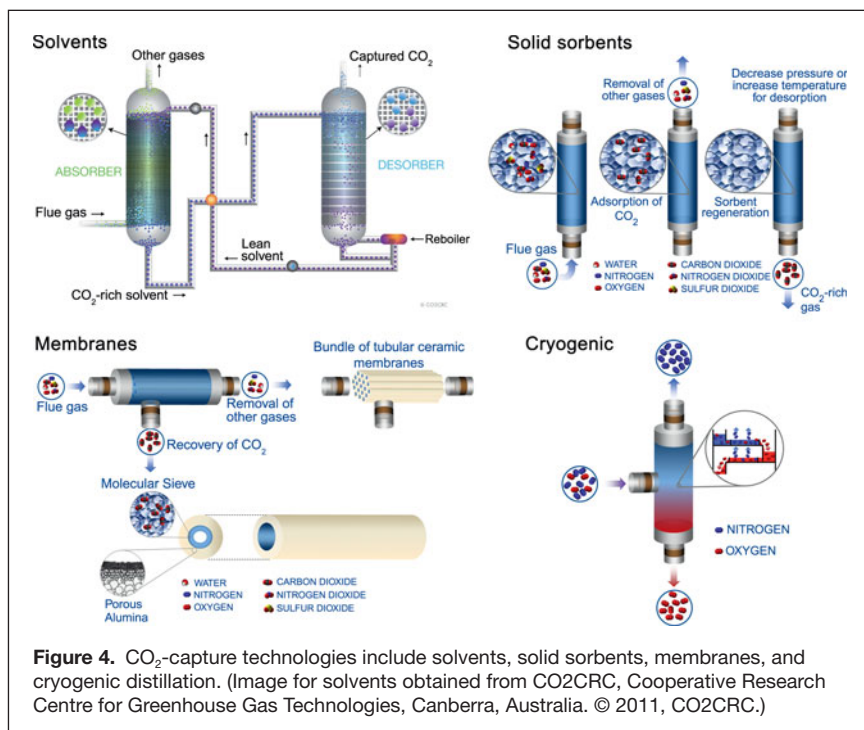
The CO<sub>2</sub>-capture research and development (R&D) program at the National Energy Technology Laboratory (NETL) of the U.S. Department of Energy (DOE) established overall targets for capture technologies of 90% CO<sub>2</sub> capture efficiency, with an associated increase in electricity costs of less than 10% for pre-combustion capture and less than 30% for post- and oxy-combustion capture.<sup>6,10</sup> Near- and long-term strategies for improving carbon capture through advanced materials science research have also been highlighted in recent reports summarizing carbon-capture workshops.<sup>11,12</sup>

### Materials for post-combustion capture

The state of the art for post-combustion carbon capture is CO<sub>2</sub> separation by chemical absorption, with solvents consisting of aqueous amine solutions that provide high absorption rates and high CO<sub>2</sub> absorption capacities.<sup>2,13</sup> However, the commercial viability of CCS is hindered by the substantial capital and operating costs of the solvent technology. In addition, amine-based solvents must contain 70 wt% water to minimize corrosion; have high heats of absorption; and are prone to thermal and oxidative degradation in the presence of common flue-gas components including O<sub>2</sub>, SO<sub>x</sub>, and NO<sub>x</sub>.

Improved solvent formulations could overcome these challenges. For example, blending the most widely used primary

Each of these CO<sub>2</sub> capture systems can employ any of the known technologies for gas separation (Figure 4). In the most mature method, a gas mixture is placed in close contact with a liquid *solvent*, and one component separates from the others as a result of differences in solubility. The differential solubility can be physical in origin, but it is often chemical. Gas separation can also be achieved by preferential adsorption on the surface of a *solid sorbent*, followed by desorption driven by changes in pressure or temperature. Another method uses a *membrane*,



**Figure 4.** CO<sub>2</sub>-capture technologies include solvents, solid sorbents, membranes, and cryogenic distillation. (Image for solvents obtained from CO<sub>2</sub>CRC, Cooperative Research Centre for Greenhouse Gas Technologies, Canberra, Australia. © 2011, CO<sub>2</sub>CRC.)

alkanolamine, monoethanolamine (MEA), with sterically hindered amines could reduce the amount of steam needed for regeneration.<sup>14,15</sup> Incorporation of promoters such as piperazine could accelerate the absorption of CO<sub>2</sub> and minimize the required concentration of amine.<sup>15–17</sup> Corrosion could also be inhibited by adding, for example, scavengers for binding with oxygen and other reaction intermediates, chelating agents for reacting with dissolved metals that take part in degradation, or heavy-metal salts that increase the ionic strength and thus decrease the oxygen solubility.<sup>18</sup> Researchers are also seeking alternative solvents, including CO<sub>2</sub>-philic ionic liquids,<sup>19–21</sup> amine-neutralized amino-acid salts,<sup>22</sup> and solvents whose viscosity and polarity change upon contact with CO<sub>2</sub>.<sup>23,24</sup>

Solid sorbents are also being explored as a way to reduce costs by avoiding the volatility and corrosion problems of aqueous amine solvents. Some of the key desired solid-sorbent properties include large surface area, strong affinity toward CO<sub>2</sub> compared to other gas constituents, low energy consumption during CO<sub>2</sub> desorption (sorbent regeneration), and high stability to moisture. A recent cost analysis of a vacuum-swing process suggested that an adsorbent with a working capacity of 4.3 mmol/g (millimoles of CO<sub>2</sub> per gram of sorbent) and a CO<sub>2</sub>/N<sub>2</sub> selectivity of 150 would reduce the capture cost to US\$30 per tonne of post-combustion CO<sub>2</sub> avoided.<sup>25</sup>

There are several candidate materials with uptakes and selectivities that are competitive with those of liquid solvents. Activated carbons have CO<sub>2</sub> uptakes up to 4 mmol/g and CO<sub>2</sub>/N<sub>2</sub> selectivities near 10 at atmospheric conditions (1 bar and room temperature).<sup>26</sup> Zeolitic materials offer CO<sub>2</sub> adsorption uptakes up to 4.5 mmol/g and much larger selectivities than activated

carbon.<sup>27</sup> However, zeolites require higher regeneration temperatures because of their sensitivity to moisture and higher heats of CO<sub>2</sub> adsorption.<sup>28,29</sup> For increased capacities and selectivities, hybrid materials are being developed by amine functionalization of pore walls in activated carbons and porous silica,<sup>30–33</sup> although further understanding of the interaction between CO<sub>2</sub> and functional amine groups is needed. Some hyperbranched aminosilicas can adsorb up to 5.5 mmol of CO<sub>2</sub> per gram at atmospheric pressure.<sup>34</sup>

An emerging class of materials called metal-organic frameworks (MOFs), constructed by bridging transition-metal nodes with organic ligands, have considerable potential as CO<sub>2</sub> sorbents, with some exhibiting CO<sub>2</sub> uptakes up to 33 mmol/g at 32 bar.<sup>35</sup> However, MOF uptakes surpass those of zeolites only at pressures higher than 10 bar. To enhance their uptake and selectivity for post-combustion-like gas streams with low CO<sub>2</sub> partial pressures, functionalization is being pursued through incorporation of CO<sub>2</sub>-philic ligands (e.g., amine-functionalized ligands)<sup>36,37</sup> or coordination to unsaturated metal centers.<sup>38,39</sup> Further details on current and emerging

CO<sub>2</sub> adsorbent materials, including the issues of thermal degradation, poisoning, attrition, and thermal management, can be found in recent review articles.<sup>40,41</sup>

Passive CO<sub>2</sub> separation using membranes is attractive because it eliminates the need for thermal or pressure cycling for regeneration.<sup>42</sup> However, membrane separation requires a pressure differential, which can be costly in atmospheric-pressure post-combustion streams with CO<sub>2</sub> concentrations below 15 vol%. The CO<sub>2</sub>-capture capability of a membrane is governed by the CO<sub>2</sub> permeability, which determines the rate at which CO<sub>2</sub> is removed from the feed gas, and the CO<sub>2</sub>/N<sub>2</sub> selectivity, which affects the purity of the CO<sub>2</sub>-containing effluent. One study found that a membrane with a CO<sub>2</sub> permeability of 300 barrer and a CO<sub>2</sub>/N<sub>2</sub> selectivity of 250 costing US\$10/m<sup>2</sup> would reduce the capture cost below US\$25 per tonne of post-combustion CO<sub>2</sub> avoided.<sup>43</sup>

Several inorganic and organic membrane materials are being considered for post-combustion capture. Molecular-size sieving is a common mechanism for gas separation, but the similar kinetic diameters of CO<sub>2</sub> (3.30 Å) and N<sub>2</sub> (3.64 Å)<sup>44</sup> make this approach very challenging. Another difficulty is the design of chemically stable membranes compatible with large-scale fabrication. Although large-area polymeric membranes are easily fabricated, their size-sieving ability can be reduced by polymer swelling when CO<sub>2</sub> is present.<sup>45</sup> Inorganic membranes are more chemically stable in the presence of CO<sub>2</sub>, but they are hard to fabricate at a large scale. One approach that could combine the strengths of the two technologies is the dispersion of inorganic particles into a continuous polymeric base membrane.

Functionalization of pore walls with CO<sub>2</sub>-philic compounds is also being evaluated to increase CO<sub>2</sub>/N<sub>2</sub> selectivity.<sup>46</sup> Amine



functionalization of some zeolite-based membranes can increase the CO<sub>2</sub> separation index (a measure that combines selectivity and permeability) by more than 150%<sup>47</sup> and can raise the CO<sub>2</sub>/N<sub>2</sub> selectivity of the bare polymeric membrane.<sup>48</sup> Introduction of magnesia into alumina-based membranes has been explored to induce the preferential surface diffusion of CO<sub>2</sub>.<sup>49</sup> Beyond molecular-size sieving, research is also exploring the separation of gas molecules based on their relative solubilities in membranes, where gas molecules can cross the membrane through a solution–diffusion transport mechanism.<sup>50,51</sup> Incorporation of CO<sub>2</sub>-philic ionic liquids into membrane assemblies is being used to facilitate the transport of CO<sub>2</sub> molecules.<sup>52</sup> A recent topical report on CO<sub>2</sub>-selective membranes provides further details on a wide range of membrane materials.<sup>53</sup>

### Materials for oxy-combustion capture

Oxygen separation from air by cryogenic distillation is a mature technology. However, alternative materials and approaches are being explored to inexpensively produce the vast quantities of pure O<sub>2</sub> needed for CCS. For O<sub>2</sub> sorbents, for example, efforts center on increasing the framework stability and decreasing the energy required for oxygen desorption.

For solid sorbents, O<sub>2</sub> separation from N<sub>2</sub> using molecular-size sieves is challenging because of the similar kinetic diameters of these molecules, 3.46 Å (O<sub>2</sub>) and 3.64 Å (N<sub>2</sub>).<sup>44</sup> Hybrid composite materials provide additional separation mechanisms, for example, through the incorporation of transition-metal complexes that reversibly bind to O<sub>2</sub> with high specificity.<sup>54–56</sup> The intrinsic exposed metal sites in some MOFs, such as Cr(II)-based MOFs, also allow for selective binding to O<sub>2</sub> over N<sub>2</sub>.<sup>57</sup>

Ceramic- and polymer-based oxygen-capture materials are also being considered in membrane configurations. The most commonly used polymeric membranes exhibit physical aging, which reduces overall gas permeability but increases O<sub>2</sub> sensitivity.<sup>58</sup> Hemoglobin-inspired polymeric membranes containing cobalt complexes are being explored to increase the O<sub>2</sub>/N<sub>2</sub> selectivity by reversibly binding with molecular oxygen.<sup>59</sup> Metal complexes have also been incorporated into alumina–zeolite composite membranes to improve oxygen selectivity.<sup>60</sup>

Mixed metal oxide membranes are also being used to separate oxygen from air by virtue of oxygen ion conduction,<sup>61,62</sup> which could enable the integration of oxygen separation and combustion in one unit. As an alternative to oxygen extraction from air, transition-metal oxide particles can be employed as oxygen carriers, in a process known as chemical-looping combustion, in which the metal oxide goes through oxidation/reduction cycles between two reactors. Deposition of the active metal oxides onto inert supports made of silica and alumina is being studied to increase the reactivity and durability of the metal oxide particles.<sup>63</sup>

### Materials for pre-combustion capture

To separate CO<sub>2</sub> from H<sub>2</sub>-rich gasification-derived gas streams, absorption using physical solvents based on methanol or mixtures of dimethyl ethers of polyethylene glycol has been the most common method. Physical solvents are highly efficient

in capturing CO<sub>2</sub> at high partial pressures and temperatures between –60°C and 40°C, depending on the nature of the solvent.<sup>6</sup> Research efforts are focused on developing solvents that can operate closer to the 200–400°C temperatures of the water–gas shift reaction and thus reduce the energy penalties associated with temperature cycling.<sup>64</sup>

Apart from solvents, several solid sorbents and membranes are being considered for pre-combustion. Porous materials containing CO<sub>2</sub>-philic functional groups have shown great promise for CO<sub>2</sub>/H<sub>2</sub> separation. For example, MOFs with surfaces containing exposed metal-cation sites outperform the CO<sub>2</sub> uptakes of zeolite 13X (a common molecular sieve) at pressures between 5 bar and 40 bar, while retaining comparable heats of adsorption.<sup>65</sup>

CO<sub>2</sub> can also be separated from a CO<sub>2</sub>/H<sub>2</sub> mixture through solution–diffusion in dense membranes. Integration of specific ionic liquids into polymeric membranes has been reported to preferentially facilitate the transport of CO<sub>2</sub> over H<sub>2</sub>. The low vapor pressure and high thermal stability of ionic liquids make them suitable for high-temperature applications,<sup>52,66</sup> but support materials with higher thermal stability than porous polymers will be needed. For high-temperature applications, adsorption of CO<sub>2</sub> onto basic sites in alkaline-earth oxides (e.g., CaO, MgO) is being explored. Although the CO<sub>2</sub> adsorption uptake of CaO (~1.092 g of CO<sub>2</sub> per gram of sorbent) is larger than that of MgO (~0.785 g/g) at high temperatures, regeneration of MgO requires less energy.<sup>67</sup>

The anionic clays known as hydrotalcites represent another class of materials suitable for CO<sub>2</sub> adsorption at temperatures of 400–500°C. Impregnation with K<sub>2</sub>CO<sub>3</sub> has been reported to enhance the CO<sub>2</sub> uptakes in these materials.<sup>68,69</sup> Both alkaline-earth oxides and hydrotalcites degrade after several cycles, but the regeneration ability of hydrotalcites can be improved through variations in the calcination step.<sup>70</sup> Lithium-containing oxides, such as Li<sub>2</sub>ZrO<sub>3</sub> and Li<sub>4</sub>SiO<sub>4</sub>, have also gained considerable attention for high-temperature CO<sub>2</sub> sorption.<sup>71,72</sup> Further details on sorbent materials for pre-combustion can be found in References 40 and 41.

An alternative to extracting the CO<sub>2</sub> from gasification-based streams is removing the H<sub>2</sub>. Such processes already produce clean streams of hydrogen for use as fuel in integrated gasification combined cycle (IGCC) plants or as a feedstock in the production of chemicals. They leave behind a CO<sub>2</sub>-rich gas under high pressure, which would facilitate the CO<sub>2</sub> compression needed for transport and storage. Because of the slightly smaller kinetic diameter of H<sub>2</sub> (~2.89 Å) compared to CO<sub>2</sub> (~3.30 Å), molecular-size sieving has been used for H<sub>2</sub>/CO<sub>2</sub> separation. Porous amorphous silica and zeolite membranes have shown good H<sub>2</sub> selectivity with respect to other gases.<sup>73</sup> Progress is being made to avoid structural defects, reduce fabrication costs, and increase operational stability. Zeolitic imidazole frameworks, a subset of MOFs, supported on porous alumina substrates have been reported to have adequate H<sub>2</sub>/CO<sub>2</sub> selectivities and exceptional hydrothermal stability up to 500°C.<sup>74</sup>



To facilitate membrane fabrication with inorganic components and overcome the selectivity/permeability tradeoffs imposed by bare polymeric membranes, hybrid membrane composites are being evaluated.<sup>75,76</sup> Integration of layered silicate into a porous polymeric substrate doubles the H<sub>2</sub>/CO<sub>2</sub> selectivity compared to that of the bare substrate at 35°C.<sup>77</sup> Other materials used commonly for hydrogen separation are dense (nonporous) inorganic membranes that can selectively separate hydrogen through a solution–diffusion mechanism and withstand elevated temperatures.<sup>78</sup> High-purity hydrogen can be obtained with dense palladium-based membranes. However, because of the high cost of pure bulk palladium membranes, efforts have focused on developing composites through the deposition of a thin layer of palladium or palladium alloy onto a porous support.<sup>79–81</sup> Further information on membrane materials can be found in Reference 53.

### Prospects for capture materials

Solvent-free technologies such as solid sorbents and membrane materials for post-, oxy-, and pre-combustion applications can, in principle, be engineered with specific physical and chemical functionalities to meet carbon-capture performance targets. Systematic approaches to the rapid design and assessment of these materials with respect to gas selectivity, regeneration ability (for sorbents), gas permeance (for membranes), and scale-up potential are essential. One challenge relates to the complex dynamic response of some of these materials to stimuli such as temperature, pressure, and gas composition, which makes characterization of the interaction between a particular gas and solid material “in action” very difficult. A multidisciplinary team of scientists at the National Institute of Standards and Technology (NIST), in collaboration with NETL, has begun to develop sophisticated *in situ* measurements to address this issue.<sup>82</sup>

### Compression, transportation, and geological storage

Once the capture step has been completed, the CO<sub>2</sub>-rich gas must be compressed to approximately 100 bar to reach a liquid or dense state. This compression facilitates its transportation by pipelines or ships to a suitable location for long-term storage.

### Compression and transportation materials

As mentioned earlier, almost one-quarter of the increase in electricity costs from post-combustion capture comes from compression, transportation, and storage of CO<sub>2</sub> and post-injection monitoring.<sup>9</sup> The energy required for compressing and pumping CO<sub>2</sub> depends on its thermodynamic and flow properties, which are affected by any impurities remaining after capture (e.g., O<sub>2</sub>, water, SO<sub>x</sub>, and NO<sub>x</sub>).<sup>3</sup> Water and oxygen in the CO<sub>2</sub> stream restrict the range of suitable compressor and pipeline materials, because they increase corrosion. CO<sub>2</sub> pipelines, typically made of carbon steel, have already been extensively used to transport clean, dry CO<sub>2</sub> for enhanced oil recovery applications,<sup>3,83</sup> but the corrosion rate increases significantly as CO<sub>2</sub> dissolves and

ionizes in water to form a weak acid. Using corrosion-resistant alloys or purifying the CO<sub>2</sub> stream can be very expensive. The relationship between impurity levels, materials performance, and cost must be understood to design the large networks of compression equipment and pipelines needed for carbon mitigation.<sup>84</sup>

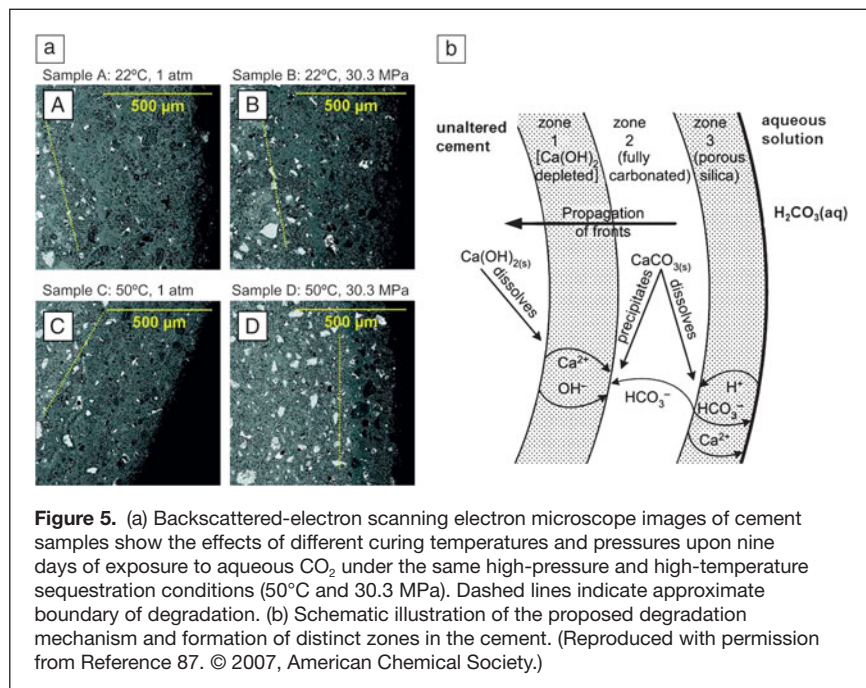
### Materials for geologic storage

Geologic storage of CO<sub>2</sub> entails injection of dense or supercritical CO<sub>2</sub> into deep underground formations, such as depleted oil and gas fields, saline formations, and deep coal seams, for permanent storage. Efficient CO<sub>2</sub> storage can be achieved in the pores of sedimentary rocks because CO<sub>2</sub> has a liquid-like density at depths of 800–1000 m, depending on the vertical temperature gradient.<sup>85</sup>

Geologic storage of anthropogenic CO<sub>2</sub> builds on a fundamental understanding of earth science, decades of oil and gas industry practice, and extensive experience with injecting CO<sub>2</sub> underground for enhanced oil recovery. Injection at scales of 6 Mt of CO<sub>2</sub> per year from non-power-plant sources has been demonstrated, and larger projects storing CO<sub>2</sub> from fossil-fuel power plants are underway. More than eight projects currently store CO<sub>2</sub> from pilot-scale (<80 MW) fossil-fuel power plants worldwide, and about 20 large-scale projects will come online over the next decade to store CO<sub>2</sub> from power plants generating up to 1200 MW each, on the order of 10 Mt of CO<sub>2</sub> per year.<sup>86</sup>

From the materials perspective, there is a great need to understand the kinetics of geochemical trapping, the long-term impact of CO<sub>2</sub> on pore fluids and mineral rocks, and the effects of CO<sub>2</sub> adsorption and CH<sub>4</sub> desorption on coal seams. Further, solid plugs made of steel and cement, typically used to seal boreholes drilled through the cap rock, can degrade in the acidic CO<sub>2</sub> storage environment over the extensive lifetimes of CO<sub>2</sub> wells. For example, details such as curing conditions affect the chemical stability of cement upon exposure to a simulated CO<sub>2</sub> storage environment. **Figure 5a** shows backscattered-electron scanning electron microscope images of cement samples cured at different temperatures and pressures and then exposed to aqueous CO<sub>2</sub> under high-pressure and high-temperature conditions (50°C and 30.3 MPa) for nine days. The extent of cement degradation, as indicated by the dashed lines, depends on the curing conditions prior to exposure to the simulated CO<sub>2</sub> storage conditions. **Figure 5b** illustrates the proposed cement degradation mechanism, involving dissolution of CO<sub>2</sub> and calcium migration.<sup>87</sup>

Developing low-cost corrosion-resistant cements and piping materials and improving *in situ* methods for characterizing their conditions over time are critical for controlling the risk of leakage. Mechanistic studies of the interactions between CO<sub>2</sub>, surrounding fluids, and wellbore materials under geological storage conditions are of great importance.<sup>88</sup> Impurities such as H<sub>2</sub>S, SO<sub>2</sub>, and O<sub>2</sub> in the CO<sub>2</sub> stream change its behavior. They can increase the risk of formation plugging and jeopardize well integrity by supporting precipitation, mineral dissolution, or biofouling, and they also present an environmental risk if



requires extensive data on geological sites and the geochemical interactions between impure  $\text{CO}_2$  and the natural and engineered materials in the intended storage media.

Research and development efforts in multiple laboratories worldwide are underway to reduce the costs of CCS technologies for commercial development. Advancing materials in this challenging field presents an exciting opportunity for the scientific community to put manufacturing and fossil-fuel energy generation on a more sustainable path.

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contamination of an underground source of drinking water occurs.

Studies under the NETL R&D program on carbon-storage technologies consider 11 types of geologic formations and two classes of geologic seals. They will investigate the effects of  $\text{CO}_2$  injection on fluids, minerals, seals, and faults or fractures in the formations; improve understanding of cap-rock integrity; refine predictive models of  $\text{CO}_2$  movement after injection; and evaluate the prospects of permanently storing  $\text{CO}_2$  through mineralization.<sup>10</sup> A multiyear information-exchange program at the Electric Power Research Institute (EPRI) aims to determine the purity level of  $\text{CO}_2$  required for maximum injection rate and capacity in a particular basin that avoids potential contamination of underground sources of drinking water by storage operations.<sup>84</sup>

## Conclusions

Several opportunities are available for materials scientists to help manage atmospheric  $\text{CO}_2$  through reduction of  $\text{CO}_2$  emissions from point sources. Cost-efficient solvents, sorbents, and membranes with better carbon-capture performance will have a profound impact on the sustainable use of fossil-fuel-based energy and the fabrication of products. Although the manufacture and operating costs of sorbents and membranes can be improved through advances in materials science, widespread adoption will take time.<sup>89</sup> Predicting how improvements at the laboratory scale will translate into overall savings in electricity and/or product manufacturing costs is an enormous challenge.

Beyond  $\text{CO}_2$  capture, materials optimization is needed to extend the lifetime of compression equipment and pipelines that contact  $\text{CO}_2$  from power plants or industry. Reliable assessment of geological locations for long-term  $\text{CO}_2$  storage worldwide



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