PCO$_2$R Partnership
Plains CO$_2$ Reduction (PCOR) Partnership
Energy & Environmental Research Center (EERC)

CURRENT STATUS OF CO$_2$ CAPTURE TECHNOLOGY DEVELOPMENT AND APPLICATION

Value-Added Report

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ABSTRACT

The Energy & Environmental Research Center has prepared an overview of the current status of carbon capture technology development and application. The overview covers technologies that apply to the three combustion platforms: precombustion, during combustion (oxycombustion and chemical-looping combustion), and postcombustion. The technologies reviewed fall into the categories of physical and chemical absorption; physical and chemical adsorption; oxygen-, hydrogen-, and carbon dioxide-CO$_2$-permeable membrane processes; cryogenic processes; mineralization; and photosynthesis and chemical and biochemical reduction processes. The document provides an overview of the technical basis for each separation technique and information on nearly 100 technologies and/or research efforts.

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NOMENCLATURE

AAP	advanced amine process
ADA–ES	ADA–Environmental Solutions
ADEME	French Environment and Energy Management Agency
AEP	American Electric Power
AHPC	activated hot potassium carbonate
aMDEA	activated methyldiethanolamine
Ar	argon
ARPA-E	Advanced Research Projects Agency – Energy
As	arsenic
ASU	air separation unit
atm	atmosphere
ATMI	Advanced Technology Materials, Inc.
AVS	Antelope Valley Station
AZEP	advanced zero emission power plant
Btu	British thermal unit
°C	degree Celsius
CA	carbonic anhydrase
$CaCO_3$	calcium carbonate
CaO	calcium oxide
CAP	chilled ammonia process
CCC	cryogenic carbon capture
CCP	CO_2 Capture Project
CCPI	Clean Coal Power Initiative
CCS	carbon capture and storage
CDCL	coal direct chemical looping
CFCMS	carbon fiber composite molecular sieve
CFZ	controlled-freeze zone
CLC	chemical-looping combustion
CMR	catalytic membrane reactor
CO	carbon monoxide
CO_2	carbon dioxide
COE	cost of electricity
COS	carbonyl sulfide
CSM	Colorado School of Mines
CTI	Cansolv Technologies, Inc.
DCC	direct-contact cooler
DEA	diethanolamine
DEP	Department of Environmental Protection
DGA	diglycolamine
DICP	Dalian Institute of Chemical Physics
DIPA	diisopropanolamine
DMC	dimethylcarbonate

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DOE	U.S. Department of Energy
DSME	Daewoo Shipbuilding & Marine Engineering Co. Ltd.
ECBM	enhanced coalbed methane
ECN	Energieonderzoek Centrum Nederland (Netherlands Energy Research Foundation)
ECO	electrocatalytic oxidation
EERC	Energy & Environmental Research Center
EET	Environmental Energy Technology, Inc.
EOR	enhanced oil recovery
EPA	U.S. Environmental Protection Agency
EPRI	Electric Power Research Institute
ESA	electrical swing adsorption
ESP	electrostatic precipitator
°F	degree Fahrenheit
FGD	flue gas desulfurization
GTI	Gas Technology Institute
H_2	hydrogen
H_2S	hydrogen sulfide
ha	hectare
HAMR	hybrid adsorption membrane reactor
HAS	hyperbranched aluminosilica
HCl	hydrochloric acid
Hg	mercury
HHV	higher heating value
hr	hour
HR	heat of reaction
HMR	hydrogen membrane reformer
IGCC	integrated gasification combined cycle
IL	ionic liquid
IMPACCT	Innovative Materials & Processes for Advanced Carbon Capture Technologies
INEEL	Idaho National Energy and Engineering Laboratory
ISGS	Illinois State Geological Survey
ITM	ion transport membrane
IVCAP	integrated vacuum carbonate absorption process
K_2CO_3	potassium carbonate
$KHCO_3$	potassium bicarbonate
kg	kilogram
KHMAS	Kvaerner Hybrid Membrane Absorption System
kJ	kilojoules
KM CDR	Kansai Mitsubishi Carbon Dioxide Recovery
kW_e	kilowatt electrical
kWh	kilowatt hour

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kW_{th}	kilowatt thermal
kPa	kilopascal
LANL	Los Alamos National Laboratory
lb	pound
LDH	layered double hydroxide
LHV	lower heating value
LP	low pressure
m	meter
m^3	cubic meter
MCM	mixed conducting membrane
MDEA	methyldiethanolamine
MEA	monoethanolamine
$MgCO_3$	magnesium carbonate
MgO	magnesium oxide
$Mg(OH)_2$	magnesium hydroxide
MHI	Mitsubishi Heavy Industries
MJ	megajoules
MMBtu	million Btu
MPCRF	multipollutant control research facility
MOF	metal organic framework
MPa	megapascal
MR	membrane reactor
MTR	Membrane Technology & Research, Inc.
MTU	mobile test unit
MVA	monitoring, verification, and accounting
MW	megawatt
MW_e	megawatt electrical
MWh	megawatt hour
N_2	nitrogen
NAM	N-acetylmorpholine
NaCl	sodium chloride
Na_2CO_3	sodium carbonate
$NaHCO_3$	sodium bicarbonate
NaOH	sodium hydroxide
NETL	National Energy Technology Laboratory
NFM	N-formylmorpholine
NH_3	ammonia
Nm^3	normal cubic meter
NMP	N-methyl-2-pyrrolidone
NO_2	nitrogen dioxide
NO_x	nitrogen oxides

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NOMENCLATURE (continued)

NSE	New Sky Energy
NSG	Neumann Systems Group, Inc.
NTUA	National Technical University of Athens
O_2	oxygen
ORNL	Oak Ridge National Laboratory
PAMAM	poly(amidoamine)
PBI	polybenzimidazole
pc	pulverized coal
PCCC	postcombustion carbon capture
PCO_2C	Partnership for Carbon Capture
PCOR	Plains CO_2 Reduction (Partnership)
Pd	palladium
PDC	Process Design Center
PEEK	polyether ether ketone
PFBC	pressurized fluidized-bed combustion
PNGC	pressurized natural gas combustion
PNNL	Pacific Northwest National Laboratory
POSTCAP™	Siemens Technology for postcombustion CO_2 capture
ppm	parts per million
ppmv	parts per million by volume
PSA	pressure swing adsorption
psi	pounds per square inch
psia	pounds per square inch absolute (gauge pressure plus barometric pressure, which is about 14.7 psi)
psig	pounds per square inch gauge
PTFE	polytetrafluoroethylene
PVDF	polyvinylidene fluoride
PZ	piperazine
RITE	Research Institute of Innovative Technology for the Earth
RTIL	room-temperature ionic liquid
scfd	standard cubic feet per day
SCR	selective catalytic reduction
SEWGS	sorption-enhanced water–gas shift
SO_2	sulfur dioxide
SO_3	sulfur trioxide
SO_x	sulfur oxides
SRI	Stanford Research Institute
STEP	Solar Thermal Electrochemical Photo (carbon capture)
TEA	triethanolamine
TIPS	ThermoEnergy Integrated Power System
TRE	theoretical regeneration energy
TSA	temperature swing adsorption

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NOMENCLATURE (continued)

tonne	metric ton
ton	short ton
UTRC	United Technologies Research Center
vol%	volume percent
VPSA	vacuum pressure swing adsorption
VSA	vacuum swing adsorption
WGS	water–gas shift
ZIF	zeolitic imidazolate framework

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CURRENT STATUS OF CO$_2$ CAPTURE TECHNOLOGY DEVELOPMENT AND APPLICATION

EXECUTIVE SUMMARY

Industries around the world are investigating ways to decrease their carbon footprint as concerns are raised about the effects of carbon dioxide (CO$_2$) as a greenhouse gas. These methods include improving process efficiencies so that less carbon-based fuel is used, switching to fuels with lower fossil carbon content (e.g., biomass or biomass blends, augmentation by wind or solar power), and capture of the CO$_2$ produced for either beneficial reuse or for permanent storage. CO$_2$ capture, which will be required at most, if not all, existing power generation facilities to meet the current national CO$_2$ reduction goals, is currently an expensive process. For this reason, considerable effort is being focused on the development of more efficient, cost-effective capture techniques. This report identifies and briefly discusses carbon capture technologies that are currently available and/or under development. The vendors who are involved in the sale and/or development of these technologies are also identified, as are the key technical references, which provide technical and economic details for those readers interested in investigating the individual capture technologies in more detail.

The CO$_2$ capture technologies that are addressed in this report are summarized in Figure ES-1, which provides an illustration of the technical approaches that can be taken to effect the capture of CO$_2$ derived from fossil fuel combustion. As shown, there are three opportunities, or platforms, for capturing CO$_2$ from fossil fuel combustion systems: before (pre), during (through combustion modification), and after (post) combustion. The specific categories of CO$_2$ capture technologies that are available for use in one or more of these platforms include absorption, adsorption, membranes, and other techniques such as mineralization, reduction, and cryogenic methods. The Plains CO$_2$ Reduction (PCOR) Partnership has gathered information on the state of the art of these CO$_2$ capture technologies as applied to each of these three platforms. Every effort has been made to provide the most comprehensive information possible, but because of the proprietary and dynamic nature of technology development, not every CO$_2$ capture technology currently under development has been included. This report summarizes most of the relevant technologies for which information is currently available.

Precombustion

Precombustion removal refers to near-complete capture of the CO$_2$ prior to fuel combustion and is usually implemented in conjunction with gasification (of coal, coke, waste biomass, or residual oil) or steam reforming/partial oxidation of natural gas to produce syngas, which contains carbon monoxide and hydrogen (H$_2$). Subsequent conversion via the water–gas shift reaction produces CO$_2$ from the CO, resulting in H$_2$-rich syngas. This syngas (often with

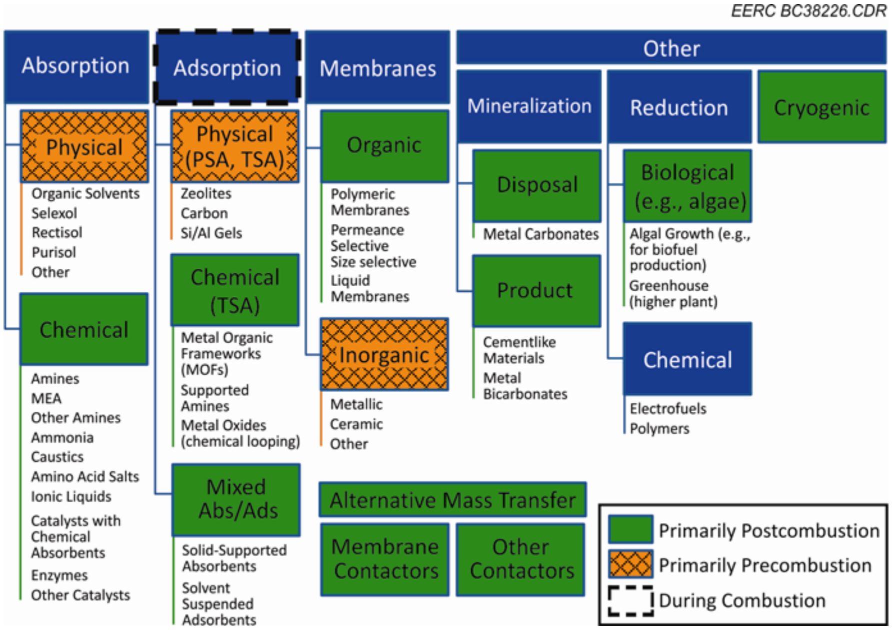

Figure ES-1. Carbon capture technology categories.

nitrogen added for temperature control) can be combusted in gas turbines, boilers, or furnaces. Purified H_2 can be used in fuel cells.

Typical CO_2 stream concentrations before capture are 25 to 40 volume percent at pressures ranging from 360 to 725 psia. This high partial pressure of CO_2, relative to that of combustion flue gas, enables separation using physical solvents. A physical solvent utilizes the pressure-dependent solubility of CO_2 in the solvent (as opposed to a chemical reaction with the solvent) to separate the CO_2 from the mixed-gas stream. Processes being developed for using physical adsorbents (e.g,. zeolites, activated carbon), chemical adsorbents (e.g., metal oxides and metal hydroxides), and membrane systems including those that are selectively permeable to oxygen, hydrogen, or carbon are commercially applied in the gas-processing industries, and some are at small pilot demonstration scale for use in CO_2 capture, but most are currently at the research and development stage.

The majority of the commercial capture technologies, e.g., Selexol™, Rectisol®, and Purisol®, were developed in the mid-1900s and were utilized for acid gas (hydrogen sulfide and CO_2) removal by the early developers of commercial synthetic fuel (synfuel)-manufacturing plants (such as coal gasification). Hence, these technologies were an integral part of the synfuel demonstration tests that were conducted by the Synthetic Fuels Development Corporation in the early 1980s. The Synthetic Fuels Development Corporation was a U.S. government-funded corporation established in 1980 by the Synthetic Fuels Corporation *Act* to create a financial bridge for the development and construction of commercial synthetic fuel-manufacturing plants in the United States. The efforts of the corporation focused heavily on the execution of demonstration tests of coal conversion technologies throughout the country, including the Great Plains Synfuels Plant in Beulah, North Dakota. The corporation was abolished in 1985 as a result of the drop in worldwide oil prices that occurred in the early 1980s. Similarly, the use of alkanolamines for acid gas management is also at a commercial scale, having been developed early in the 20th century, with the first patent granted in 1930. This long history of large-scale/commercial applications of these gas purification technologies has placed them as clear front runners for the precombustion capture of CO_2.

During Combustion

With process modification, a concentrated stream of CO_2 can be generated during combustion in a process called oxygen combustion, or oxycombustion. Substitution of pure oxygen for the combustion air produces a CO_2-rich flue gas that requires minimum processing before use or permanent storage. Typically, the CO_2 can be recovered by compressing, cooling, and dehydrating the gas stream to remove traces of water that are generated during combustion. When the end use requires it, any noncondensable contaminants that may be present such as N_2, nitrogen oxides oxygen (O_2,) and argon can be removed by flashing in a gas–liquid separator.

The oxycombustion processes that are being developed include technologies represented by modified or retrofitted combustion units, new combustion units, and other processes that incorporate membranes into the combustion chamber (advanced zero emission power plant), combine high-pressure combustion and exhaust gas condensation (ThermoEnergy Integrated Power System), or utilize oxygen provided by metal oxide oxygen carriers to combust the fuel (chemical looping). Oxycombustion can be performed at elevated temperature which requires the use of specially designed combustion chambers (new construction) or with the recirculation of flue gas so that combustion temperatures are controlled at or near those typically used in air-fed boilers. Recirculated flue gas-based oxycombustion has the potential to be applied as a retrofit technology, but its application will require eliminating virtually all leakage of air into the combustion chamber and flue gas treatment path. Chemical-looping combustion (CLC) technologies use solid oxidant materials (e.g., metal oxides) that are recirculated from air-contact chambers to the combustion chamber through the use of moving beds or circulating fluidized beds. It is unlikely that CLC will be applied as a retrofit technology. All of the "during combustion" technologies are currently in the developmental stage.

Besides the combustion unit retrofits, which are necessary to accommodate the higher temperatures that occur during combustion in an oxygen-rich environment or to allow for flue gas recirculation as the dilution gas, the other processes are all under development at the large pilot scale or below. For example, many groups are conducting chemical-looping development studies, which include applications to the combustion of coal, petroleum coke, natural gas, and syngas as well as use in syngas and hydrogen production and incorporation into integrated gasification combined. ALSTOM has run a successful pilot-scale, 10-lb/hr chemical-looping coal combustion system and is currently involved in scaling this to 1000 lb/hr. At the same time, Eltron Research and Development has been awarded a Phase I Small Business Innovation Research project funded by the U.S. Department of Energy (DOE) that will develop an advanced coal gasification system based on the use of chemical looping.

In addition to the previously discussed developments, there is also a need to optimize the separation of oxygen from air, minimizing the parasitic power load associated with this unit operation of oxycombustion. Relative to coal gasification, combustion requires up to three times the amount of pure oxygen. The air separation unit capacity and its associated parasitic power load are commensurately larger. Separation of oxygen from air is expensive and is currently performed at very large scale by cryogenic distillation. Other methods of separating oxygen for use during oxycombustion are being developed, most notably oxygen or ion transport membranes. These membranes operate at temperatures of roughly 500°C, meaning that oxygen separation can be integrated with the combustion process, providing a theoretically significant reduction in parasitic power loss and O_2 production cost. Oxygen transport membranes are under development by Praxair and ALSTOM Power, while an ion transport membrane process is being developed by Air Products and Chemicals. Eltron Research and Development is an ion transport membrane technology developer that has developed both O_2-permeable and H_2-permeable membranes.

Postcombustion

The most common CO_2 separation platform is postcombustion, where the CO_2 is removed from low-pressure, low-CO_2-concentration flue gas following other pollution control devices. Several types of postcombustion processes have been and are being developed to separate and remove the CO_2 from a flue gas stream, such as absorption, adsorption, membrane, and cryogenic processes and other methods that include mineralization for either disposal or to produce a mineral product and reduction to produce beneficial products such as fuels and/or plastics.

Postcombustion technologies range in scale. There are commercial processes that have been in use for acid gas management for many years. Some research processes are undergoing either pilot- or demonstration-scale testing. Current early-phase research and development processes involve small-scale testing of new chemicals, catalysts, membranes, and/or process configurations. Postcombustion capture technologies are critically important to meeting the national CO_2 emission reduction goals because they are the technologies that can be applied to the existing power generation fleet. Implementation of this emission control strategy can begin immediately through the application of available commercial technologies, but it is critical that parallel efforts continue to further optimize these technologies to improve both CO_2 capture efficiency and cost. Also of critical importance is the continued development of innovative techniques that are less capital- and energy-intensive, are amenable to in-plant retrofits, and can produce usable by-products from the captured CO_2.

The following paragraphs describe some of the postcombustion technologies that could be applied to CO_2 capture from combustion systems. It is important to note that some of the technologies listed here could also be applied to precombustion applications.

Absorption

Absorption systems that are used to capture CO_2 include physical solvent-based absorption systems that would be applicable for precombustion applications and chemical solvent-based absorption systems for precombustion and postcombustion applications. The most typical system design for both physical and chemical solvent use involves contacting the lean solvent and the CO_2-containing gas stream in an absorption tower. The loaded, or rich, solvent is then regenerated. Physical solvents can be regenerated through pressure reduction and/or heating. Chemical solvents are generally regenerated by heating, which reverses the reaction and releases the CO_2. The CO_2-lean solvent is then recirculated for reuse. Amines are the most commonly used chemical absorbent for CO_2 separation from mixed-gas streams. The baseline amine is monoethanolamine (MEA).

Other chemical absorption systems are being developed to improve the cost-effectiveness of CO_2 capture through higher CO_2 absorption capacities, faster CO_2 absorption rates, reduced solvent degradation, reduced solvent corrosiveness, and lower-regeneration energy requirements. These development and/or optimization efforts, which typically are amine- or ammonia-based, range from bench to pilot scale.

New developments in the area of chemical absorption include the use of additional solvents in absorber–stripper systems, the use of enzyme-based and enzyme-inspired catalysts, the development of new absorbents for CO_2 capture, and the development of mass-transfer devices other than absorption towers.

Adsorption

Adsorption CO_2 capture technologies remove CO_2 from mixed-gas streams onto the surface of solid sorbents. These sorbents generally have very high porosity, and therefore, high surface areas are available per unit mass and per unit volume. As is the case with absorption, adsorption can be a simple phase-partitioning physical adsorption or it can involve a chemical reaction between the sorbent and CO_2. Regeneration of the sorbent beds is typically performed by temperature or pressure swing techniques, although work is being performed on electrical swing adsorption processes.

Mixed Absorption–Adsorption

Mixed absorption–adsorption processes are those that employ a liquid absorbent (typically a chemical absorbent) trapped in or on the solid support. These are often classified with adsorption processes because they employ similar gas–solid contact arrangements (fixed-bed, fluid-bed, or moving-bed reactors), but the actual capture process occurs in a liquid layer or liquid droplet contained on or in the support. Most commonly, the chemical sorbent is an amine, although ionic liquids are likely candidates for this type of use.

Membrane Processes

Membranes employ a permeable barrier between two fluid-phase zones. This permeable barrier provides selective transport of CO_2 or other gas component. Desirable membranes are highly selective and have a high permeability for the molecule to be transported. Development of successful membrane processes involves not only selection of membrane materials with favorable properties but also the development of the physical devices or membrane modules that allow the membranes to be used and the processing system in which the membrane module is employed.

Polymer membranes can also be used for postcombustion CO_2 capture and lower-temperature H_2/CO_2 separations. These processes are a hot topic and were recently given considerable attention in a special issue of the *Journal of Membrane Science* that was dedicated to the topic “Membranes and CO_2 Separation.” The conclusions that may be reached from review of the papers is that, while membrane-based postcombustion CO_2 capture has not yet developed to the point where it can be commercially applied, the advances being made in materials, modules, and process design show promise that membrane processes will play a role in the future.

Cryogenic

In cryogenic CO_2 capture, a mixed-gas stream is compressed, and the heats of compression and condensation are removed. The stream can be 1) compressed to about 1100 psia, with water used to cool the stream; 2) compressed to 250–350 psia at 10° to 70°F, dehydrated using activated alumina or silica gel, and the condensate distilled in a stripping column; or 3) dehydrated and cooled to even lower temperatures (−78.5° to −109°F or lower) in order to condense the CO_2.

Mineralization

CO_2 capture by mineralization occurs when the CO_2 forms a stable mineral carbonate or bicarbonate. Typically, these materials are formed using calcium and magnesium cations. The end products of the mineralization processes can either be disposed of, sold as a product, or used to generate another useful product such as aggregate or a type of cement. Several organizations are investigating this approach to carbon sequestration, with the goal of generating revenues to offset the costs of CO_2 capture and sequestration.

Reduction

Reduction is the chemical transformation of the CO_2 to a reduced state through the input of energy. This concept incorporates the conversion of CO_2 into an organic compound such as a polycarbonate plastic, a fuel, or some other desired product. The process makes sense from an energy balance perspective only when the product is of high value, the fuel is effectively an energy storage product made from an intermittent energy supply source (e.g., wind, solar), and/or the fuel produced is useful in ways that the original source fuel was not (e.g., production of a transportation fuel from coal-derived CO_2). While many projects dealing with the beneficial reuse of CO_2 will use precaptured and prepurified CO_2, some projects will be focused on the direct capture of the CO_2 from flue gas (after removal of common contaminants).

CO_2 capture also can be coordinated with reduction of CO_2 to a beneficial use product. This approach is being performed and/or investigated in closed-environment agriculture for growth of flowers and food crops and in coordination with the growth of algae, microalgae, and cyanobacteria used in the production of biofuels. The reducing equivalents for these processes are provided through the photosynthetic capture of solar energy.

Evaluation of Capture Technologies

The Partnership for CO_2 Capture at the Energy & Environmental Research Center is a multiclient-funded (DOE, utility, and industry participants) program separate from the PCOR Partnership that is focused on CO_2 capture technology testing, demonstration, and development. Oxycombustion and postcombustion testing capabilities were added to an existing fuel-flexible combustion test unit (coal, natural gas, biomass). This system already included a selective catalytic reduction unit, an electrostatic precipitator, a fabric filter, wet flue gas desulfurization, and a spray dryer absorber as well as facilities for testing ash fouling, flame behavior, and other aspects of concern with respect to coal combustion. Oxycombustion tests using pure O_2 and recycled flue gas yielded flue gas CO_2 concentrations as high as 85% and over 90% for short periods of time. The retrofit for postcombustion capture included the addition of a solvent absorber–stripper system for CO_2 capture. Three solvents have been tested to date: MEA as a base case, a mixture of methyldiethanolamine MDEA and piperazine, and a proprietary solvent, H3-1, from Hitachi. Engineering economic analysis performed based on the experimental results from the oxycombustion and postcombustion tests revealed that the least-cost alternative in terms of both energy penalty and cost of electricity was the use of H3-1. Future work will include testing of additional solvents as well as the Neumann Systems Group contactor as an alternative to the traditional column-based absorber–stripper. Solid sorbent testing is planned as well.

Summary of Capture Technologies

Appendix A summarizes the technologies included in this Executive Summary and described in more detail in the report. The reader can use the appendix to make comparisons between technologies within various broad topics. The main body of this report includes descriptions of the various technologies that were derived from publicly available literature. For more detail about a particular technology, the reader is invited to explore the sources listed for that technology.

Conclusion

Considerable effort is being expended to develop a variety of cost-effective CO_2 capture technologies. Some technologies exist that can likely be applied in the near term, while others will require many years of development, testing, and demonstration. A few of the technologies offer the hope of being “game changers”—technologies that dramatically reduce CO_2 emissions at very low cost. Even so, there is still room for all entities with an interest or expertise in the area of CO_2 capture to be involved in addressing this critical research need as well as a vital need for continued funding in the area.

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INTRODUCTION

As concerns are raised about the effects of greenhouse gas emissions, primarily carbon dioxide (CO_2), industries around the world are investigating ways to decrease their carbon footprint. These methods include improving process efficiencies so that less carbon-based fuel is used, switching to fuels with lower fossil carbon content (e.g., biomass or biomass blends, augmentation by wind or solar power), and capture of the CO_2 produced for either beneficial reuse or for permanent storage. Because CO_2 capture is currently an expensive process, considerable effort is being focused on the development of more efficient, cost-effective capture techniques.

There are three opportunities to capture CO_2 from a fossil fuel combustion system: before, during (through combustion modification), and after combustion. This report, prepared by the Plains CO_2 Reduction (PCOR) Partnership, discusses the state of the art in CO_2 capture technologies for each of these three platforms. Every effort has been made to make it as comprehensive as possible, but because of the proprietary and dynamic nature of technology development, it is not realistic to assume that every CO_2 capture technology currently under development has been included.

CO$_2$ CAPTURE PLATFORMS

Precombustion

Precombustion removal refers to near-complete capture of CO_2 prior to fuel combustion and is usually implemented in conjunction with gasification (of coal, coke, waste biomass, or residual oil) or steam reforming/partial oxidation of natural gas to produce syngas, which contains carbon monoxide (CO) and hydrogen (H_2). Subsequent conversion via the water–gas shift (WGS) reaction produces CO_2 from the CO, resulting in H_2-rich syngas. This syngas (often with nitrogen [N_2] added for temperature control) can be combusted in gas turbines, boilers, or furnaces or, when the H_2 is sufficiently purified, used in fuel cells. Figure 1 is a flow sheet showing precombustion CO_2 capture. The ultimate precombustion CO_2 capture facility for use in power generation is an integrated gasification combined cycle (IGCC) system employing CO_2 capture. The U.S. Department of Energy (DOE) FutureGen Initiative was targeted toward building a full-scale facility that would serve as an example of the use of this process. On August 5, 2010, DOE announced FutureGen 2.0 as an advanced oxycombustion technology-

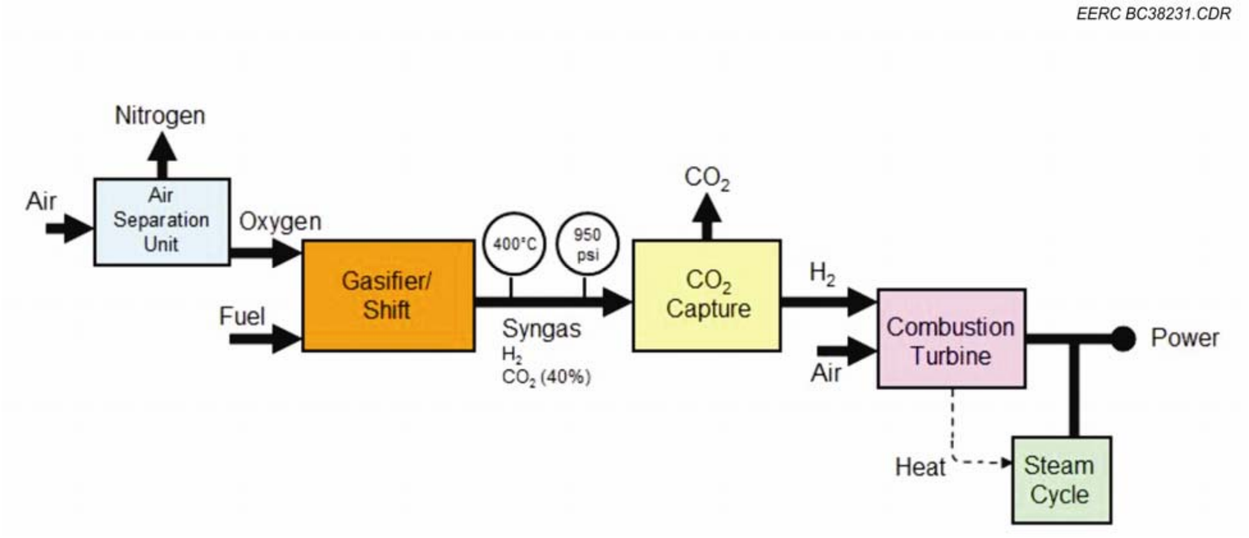

Figure 1. Schematic of precombustion CO_2 capture (taken from Figueroa and others, 2008).

based power-generation facility (U.S. Department of Energy, 2010c). Air separation units (ASUs) are commonly employed to provide oxygen for gasification and nitrogen for the dilution gas for IGCC systems.

Typical CO_2 stream concentrations before capture are 25 to 40 vol% at pressures of 363 to 725 psia, but the range can be as great as 15% to 60%, with pressures from 290 to 1015 psia (2 to 7 MPa) (Metz and others, 2005). The high partial pressure of CO_2, relative to that in combustion flue gas, enables easier separation through solvent scrubbing. Commercially available physical solvents that have been applied to precombustion CO_2 capture include UOP's Selexol™ process (UOP, LLC, 2009b), the Rectisol® process (developed independently by Linde and Lurgi) (Linde AG, 2010b; Lurgi GmbH, 2010a), and Lurgi's Purisol® process (Lurgi GmbH, 2010b). In these processes, the gas flows through a packed-tower absorber where it contacts the physical solvent and, as a consequence, acid gases such as CO_2 and hydrogen sulfide (H_2S) dissolve into the solvent. The acid gas-rich solvent flows to a second tower (stripper) where the CO_2 is released and the solvent is regenerated, usually by reducing the pressure.

In refineries and ammonia production facilities, where a lower-partial-pressure CO_2 (<220 psia, 1.5 MPa), H_2-rich syngas is produced by gas reforming, CO_2 is recovered during acid gas removal using chemical solvents such as MDEA (methyldiethanolamine, a tertiary amine) that have low regenerator heat loads. Older systems used hot potassium carbonate processes (e.g., Benfield™, CATACARB®). Modifications of these processes using promoted carbonate are more popular now. Pressure swing adsorption (PSA) is also used where high-purity hydrogen is required (UOP, LLC, 2005).

The majority of the commercial capture technologies, e.g., Selexol, Rectisol, and Purisol, were developed in the mid-1900's and were utilized for acid gas (H_2S and CO_2) removal by the early developers of commercial synthetic fuel (synfuel)-manufacturing plants (such as coal gasification) (Riesenfeld and others, 1974a). Hence, these technologies were an integral part of the synfuel demonstration tests that were conducted by the Synthetic Fuels Development Corporation in the early 1980s. The Synthetic Fuels Development Corporation was a U.S. government-funded corporation established in 1980 by the Synthetic Fuels Corporation Act to create a financial bridge for the development and construction of commercial synthetic fuel-manufacturing plants in the United States (Public Law 96-294). The efforts of the corporation focused heavily on the execution of demonstration tests of coal conversion technologies throughout the country, including the Great Plains Synfuels Plant in Beulah, North Dakota. The corporation was abolished in 1985 as a result of the drop in worldwide oil prices that occurred in the early 1980s. Similarly, the use of alkanolamines for acid gas management is also at a commercial scale, having been developed early in the 20th century, with the first patent granted in 1930 (Riesenfeld and others, 1974b). This long history of large-scale/commercial applications of these gas purification technologies has placed them as clear front runners for the precombustion capture of CO_2.

Additional CO_2 separation technologies under development for use in precombustion include high-temperature, hydrogen-permeable membranes; technologies based on the use of magnesium oxide or calcium oxide carbonation with regeneration by calcining the produced magnesium carbonate ($MgCO_3$) or calcium carbonate ($CaCO_3$) (chemical-looping process); and modification of the gasification process to include the use of a catalyst and high-temperature CO_2-selective adsorbent. One example of this is the sorption-enhanced reaction that uses a packed-bed reactor to perform steam methane reforming or the WGS reaction.

ASUs are used to supply purified O_2 for gasification. The type of ASU typically used employs cryogenic distillation of air. This is an energy-intensive process; therefore, much work is being done to develop oxygen-permeable membranes and chemical looping to supply oxygen for gasification (e.g., syngas chemical-looping process, coal direct chemical-looping [CDCL] process). Chemical looping for oxygen supply and oxygen-permeable membranes are discussed further in the section on CO_2 capture during combustion.

During Combustion

Technologies designed to allow CO_2 capture during combustion mostly fall into one of two categories: oxycombustion, where purified oxygen is supplied as the combustion gas rather than air, and chemical-looping combustion, where a solid chemical adsorbent that reacts with oxygen (metal oxide) is used to transport oxygen from an air contact reactor to the combustion chamber where the oxygen is used for combustion and the solid is returned to the air contact reactor for regeneration.

Oxycombustion

Substitution of oxygen for all of the combustion air has been proposed to produce a CO_2-rich flue gas requiring minimum separation for use or sequestration. Conventional air combustion processes in boilers or gas turbines produce flue gas that contains predominantly N_2 (>80 vol%) and excess oxygen (O_2) in addition to CO_2 and water. Separation technologies must separate CO_2 from these other components. If the air is replaced by oxygen, the N_2 content of the flue gas approaches zero (assuming minimal air leakage into the system), and the flue gas contains predominantly CO_2 along with a small amount of excess oxygen, combustion water, and other contaminants (e.g., sulfur oxides [SO_x] and nitrogen oxides [NO_x]). The CO_2 can be recovered by compression, cooling, and dehydration. The basic oxycombustion approach is shown in Figure 2.

The levels of noncondensable impurities and thermodynamics limit recovery of CO_2 and affect the purity of the product stream. The concentration of CO_2 can be targeted to a specific intended end-use application such as beneficial reuse or sequestration. For enhanced coalbed methane (ECBM) recovery, it may be acceptable to allow some constituents (e.g., N_2) to be present that would not be acceptable where a supercritical fluid is required for enhanced oil recovery (EOR) or deep reservoir injection. Where a supercritical fluid is required, noncondensable contaminants such as N_2, O_2, and argon (Ar) are removed by flashing (rapidly decreasing the pressure) in a gas–liquid separator.

There are several advantages to oxycombustion. The volume of flue gas reaching downstream systems is one-third to one-fifth that of conventional coal boilers. The process produces a flue gas stream containing more than 80 vol% CO_2, depending upon the fuel composition, purity of oxygen from the ASU, and air leakage into the boiler. Impurities such as sulfur dioxide (SO_2), NO_x, particulate, and mercury become concentrated in the flue gas, thus reducing capital and operating costs for contaminant removal. Levels of NO_x (mostly fuel-derived) may be low enough to eliminate the need for further control, and capital and operating cost savings (for control systems) may offset air separation capital and operating costs.

Just as there are advantages to oxycombustion, there are challenges to its application. Relative to coal gasification, oxycombustion requires that up to three times the amount of oxygen be supplied by the ASU. Therefore, the ASU capacity (and parasitic power load) will be commensurately larger. Separation of oxygen from air is expensive and is currently performed at

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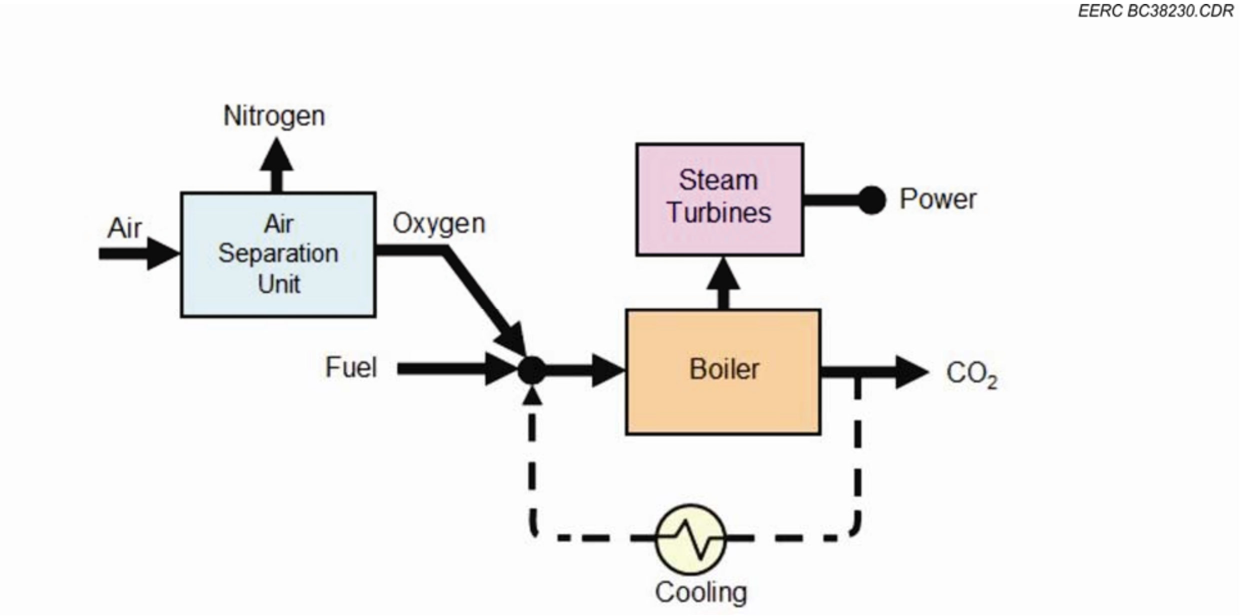

Figure 2. Schematic of an oxycombustion system (taken from Figueroa and others, 2008).

very large scale by cryogenic distillation. Other methods of separating oxygen for use during oxycombustion and gasification are being developed, most notably oxygen transport membranes and ion transport membranes. These membranes operate at temperatures of roughly 500°C, meaning that oxygen separation can be integrated with the combustion and/or gasification process, providing a theoretically significant reduction in parasitic power loss and O_2 production cost. Oxygen transport membranes are under development by Praxair and ALSTOM Power, while ion transport membranes are being developed by Air Products and Chemicals and Eltron Research and Development. These efforts are discussed further in the section on membranes found later in this report.

Other challenges that must be met include changes in heat balance that can lead to system operation at out-of-design conditions and a need to better understand gas-phase flame properties such as radiant heat transfer and flame speed (U.S. Department of Energy National Energy Technology Laboratory, 2008a). The higher combustion temperature is typically moderated through recycle of a portion of the CO_2 exhaust gas and/or gaseous or liquid water (Metz and others, 2005).

Retrofit applications would be designed to maintain the same steam outlet conditions. The higher heat capacity of the gas should potentially facilitate greater heat absorption while producing lower flue gas temperature. Higher heat absorption would result in higher boiler efficiency, but this would be offset by a higher auxiliary power load for fan power to the recycle gas used for temperature control.

Development efforts involving conventional pulverized coal (pc) testing with oxycombustion are at the scale of several hundred kilowatts and less. Developers and testing organizations include CanmetENERGY, Mitsui Babcock, American Air Liquide, Babcock & Wilcox, Foster Wheeler North America, and the Energy & Environmental Research Center (EERC).

Oxygen firing in circulating fluid-bed boilers may have an advantage over pc firing in that a significant degree of temperature control can be achieved by recirculating the solids. Lower flue gas recycle would reduce parasitic power load for fans. In addition, higher O_2 concentrations may be possible, resulting in a smaller boiler island size and reduced capital cost. Development issues center around continuous solids recirculation. Currently, testing is at the large pilot scale, with development efforts being conducted by ALSTOM Power, ABB, Praxair, and Parsons Energy.

Other processes that feature combustion in oxygen include the following:

- The advanced zero emission power (AZEP) process, being developed by ALSTOM Power, replaces the combustion chamber of an ordinary gas turbine with a mixed conducting membrane (MCM) reactor that includes a combustor, a low-temperature heat exchanger, an MCM, and a high-temperature heat exchanger. The MCM reactor separates O_2 from the air for combustion with a fuel (natural gas) (Sundkvist and others, 2001; Möller and others, 2006).

- The ThermoEnergy Integrated Power System (TIPS) process, under development by ThermoEnergy Corporation, utilizes high-pressure combustion (700 to 1300 psi) and facilitates the condensation of exhaust components such as water and CO_2 in a condensing heat exchanger (Fassbender, 2005).

Chemical-Looping Combustion

In chemical-looping combustion, there is no direct contact between the air and the fuel. The process utilizes oxygen provided by metal oxide oxygen carriers to combust the fuel, producing CO_2 and water. Once the steam is condensed, a relatively pure stream of CO_2 is produced, ready for beneficial reuse or permanent storage. Figure 3 is a schematic of a chemical-looping system. Chemical-looping development work is being performed by many groups. Current work includes application of chemical looping to combustion of coal, petroleum coke, natural gas, and syngas as well as its use in syngas and H_2 production and incorporation into IGCC. Interest in this technology is evidenced by the 1st International Conference on Chemical Looping, held in Lyon, France, in March 2010 (IFP, 2010). Conference topics included preparation and selection of appropriate oxygen carrier materials, the study of process operating conditions and performance, and process integration. Pilot testing has been performed on gaseous fuels at a scale of 50 kWth at the Korean Institute of Energy Research (Ryu and others, 2010), 120 kWth at the Vienna University of Technology (Pröll and others, 2010), and on solid fuels at scales up to 10 kWth at Chalmers University. ALSTOM has run a successful pilot-scale, 10-lb/hr chemical-looping coal combustion system and is currently involved in scaling this up to 1000 lb/hr. They have reported successful demonstration of a 65-kWth pilot and have specified a 3-MWth chemical-looping prototype system for coal combustion (Andrus and others, 2010). The

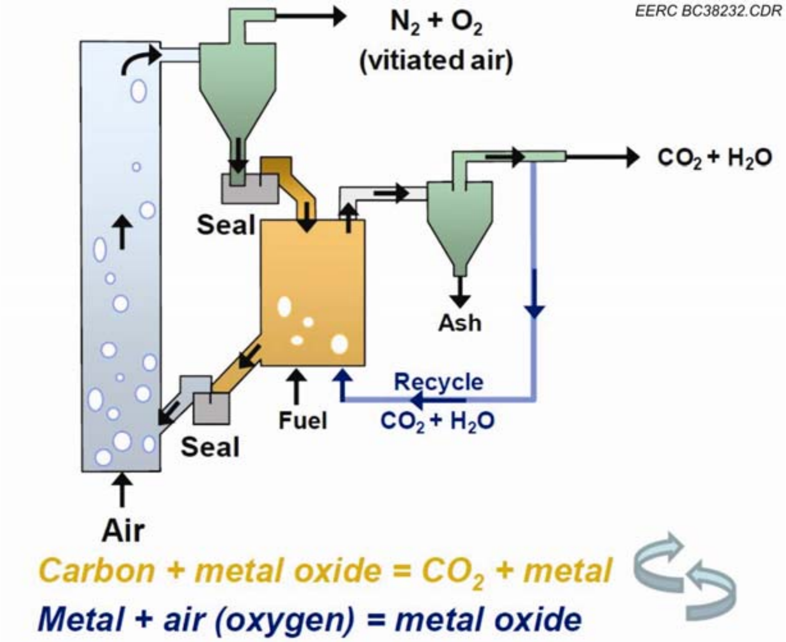

Figure 3. Chemical-looping combustion (taken from Richards and Guthrie, 2010).

metal oxide compounds used as oxygen adsorbents in chemical looping are discussed further in the section on adsorption.

Postcombustion

The most common CO_2 separation platform is postcombustion, where the CO_2 is removed from low-pressure (<2 psig), low-CO_2-concentration (<15 vol%) flue gas following the pollution control devices. Several types of postcombustion processes have been and are being developed to separate and remove the CO_2 from a flue gas stream. These include absorption, adsorption, membrane, cryogenic processes, other methods that include mineralization for either disposal or to produce a mineral product, and reduction to produce a fuel or other product (e.g., plant, algae, plastic). A schematic representing a coal-fired power plant with postcombustion capture is shown in Figure 4. The box representing CO_2 capture can contain any of a wide variety of postcombustion technologies.

In postcombustion CO_2 capture, the flue gas stream exiting the boiler contains diluents in the form of N_2 (as much as 80% of the dry gas), O_2 (2% to 8%), Ar, NO_x, and water vapor. For coal and fuel oil combustion, it will typically also contain significant quantities of SO_x, volatile metals such as mercury (Hg) and arsenic (As), and particulate. It is generally necessary to process coal, petroleum coke, and fuel oil flue gas upstream of the carbon capture process in order to control NO_x concentrations and speciation, remove most of the SO_x, and remove substantially all of the particulates and volatile metals. Flue gas from natural gas-fired boilers and natural gas- and syngas-fired turbines will generally require little to no processing upstream of the postcombustion CO_2 capture process because the fuel has been cleaned before combustion. However, these flue gas streams typically have lower CO_2 concentrations (<8% vs. <15% for coal and petroleum coke combustion) and higher O_2 concentrations, thus making capture more difficult thermodynamically.

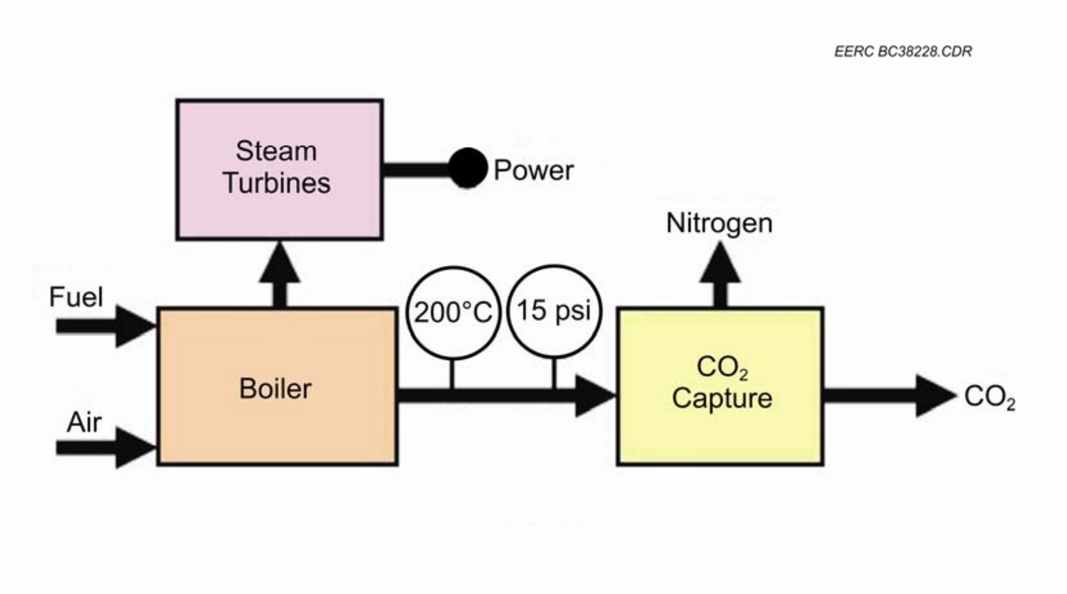

Figure 4. Schematic for postcombustion CO_2 capture (taken from Figueroa and others, 2008).

A variety of postcombustion carbon capture technologies are available. All of them would be located at the end of the pollution control system process train as follows. The boiler is fed coal and air, and NO_x emissions are controlled by boiler design and operation as well as a selective catalytic reduction (SCR) reactor, which utilizes ammonia. Sorbent and activated carbon injection are used to control mercury and other emissions, while an electrostatic precipitator (ESP) or baghouse is used to control particulate emissions, and a wet flue gas desulfurization (FGD) unit is used to control sulfur emissions. The CO_2 capture system will likely include a polishing scrubber to remove residual sulfur to very low levels (called deep sulfur scrubbing), a blower to boost the flue gas pressure sufficiently to overcome the CO_2 capture system pressure drop, the CO_2 capture technology, and dehydration and compression units needed for transportation of the CO_2 to permanent geological storage and/or for use in EOR.

Details on the postcombustion capture technologies are contained in the section covering all CO_2 capture and separation technologies. Compression, transportation, and storage are not addressed in this report.

CO_2 CAPTURE AND SEPARATION TECHNOLOGIES

Figure 5 shows the relationship between the various CO_2 capture technology types, with shading provided to indicate the most common use based on the CO_2 capture categories that have been discussed: precombustion, during combustion, and postcombustion. The specific technologies are categorized into absorption, adsorption, membranes, other, and alternative mass

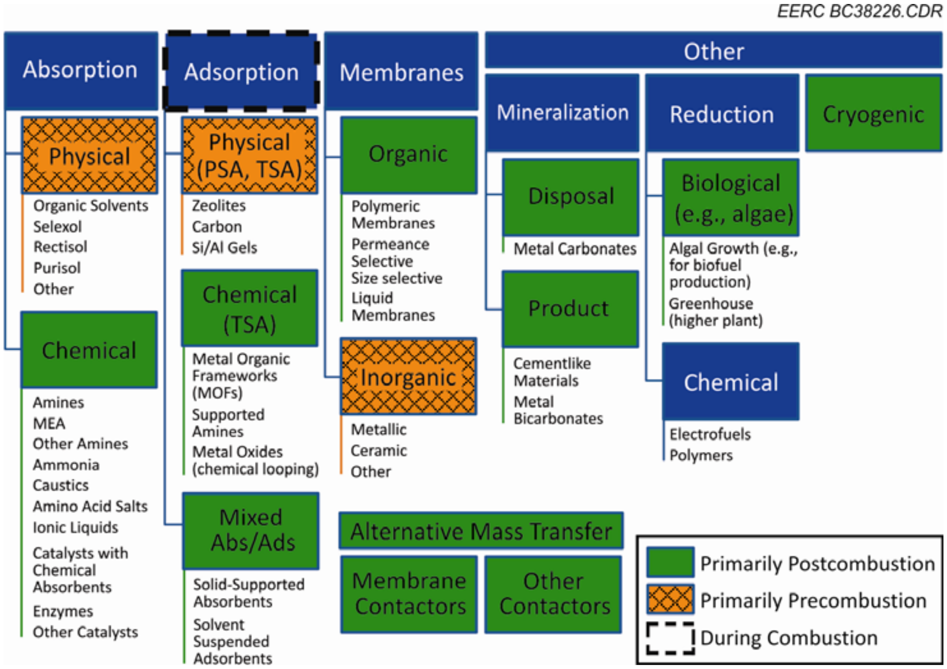

Figure 5. Carbon capture technology categories.

transfer. Absorption is broken down into physical and chemical absorption without the often-used term “mixed” because all chemical absorption includes some component of physical absorption and is, therefore, a mixed technology. Adsorption is separated into physical, chemical, and mixed adsorption, where mixed adsorption refers to solid-supported liquid absorbents. The membrane category incorporates all permeance-selective membrane systems and is divided into organic (including liquid, gel, and composite membranes) and inorganic membranes. Organic membranes are most commonly used in postcombustion applications and in the separation of CO_2 from natural gas and cooled syngas, while inorganic membranes are most commonly used in precombustion and other high-temperature separations. The category “other” has been used for mineralization and reduction methods as well as other methods such as cryogenic separation of flue gas that do not fit elsewhere. A final section on alternative mass transfer devices includes information on technologies that hold promise to decrease the size of absorber and, in some cases, stripper towers by increasing the specific surface area of gas–liquid contact (i.e., how much contact area there is in a given volume). The alternative mass transfer technology section is presented with chemical absorption.

Absorption

Absorption removes CO_2 from flue gas streams by contacting the flue gas with a solvent. Chemical and physical absorption are most commonly performed in packed-bed absorber and stripper towers. CO_2 is dissolved by the solvent and, in the case of chemical absorption, reacts to form a carbonate, bicarbonate, or carbamate associated with the chemical absorbent. Figure 6 is a diagram of flue gas scrubbing with a chemical absorbent in an absorber–stripper arrangement. CO_2-rich solvent is sent to a stripper tower where the CO_2 is released and the lean solvent is recycled back to the absorption (scrubber) tower.

Common physical solvents (which are used at high pressure) include methanol (Rectisol), dimethyl ethers of polyethylene glycol (Selexol), and N-methyl-2-pyrrolidone (Purisol). Other physical solvents such as propylene carbonate (Fluor solvent, JEFFSOL®-PC), other alkylene carbonates, and morpholine derivatives (Morphysorb®, which is a mixture of N-formyl-morpholine and N-acetyl-morpholine) are also used. Chemical CO_2 absorbents include various amines (e.g., MEA [monoethanolamine], DEA [diethanolamine], MDEA), ammonia, amino acid salts, metal carbonates, metal hydroxides, and reactive ionic liquids. Catalysts, promoters, and chemicals to protect against oxidation of the chemical absorbent and corrosion of the equipment are often added. One significant development is in the use of the enzyme carbonic anhydrase and synthetic compounds based on the reactive center of carbonic anhydrase as a catalyst.

Physical Absorption Technologies

Physical absorption processes for precombustion CO_2 capture are generally applied along with other acid gas (H_2S, carbonyl sulfide [COS]) removal methods from gasification and methane reforming (H_2 production). The ultimate precombustion CO_2 capture facility for use in power generation from coal is an IGCC employing carbon dioxide capture. It is likely that some IGCC plants that capture carbon will use physical solvent-based CO_2 capture.

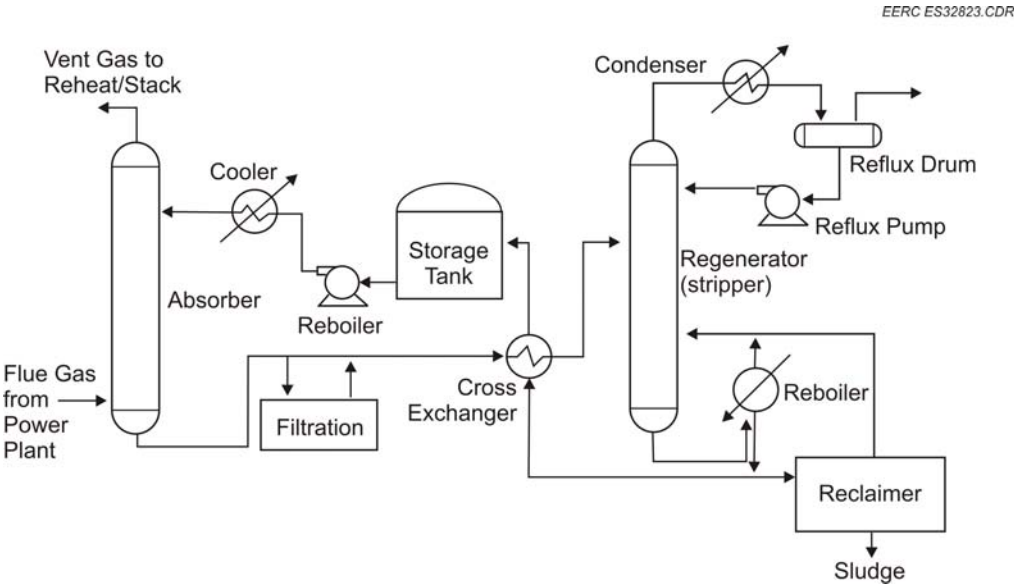

Figure 6. Chemical solvent-based absorber–stripper for CO_2 capture (taken from Jensen and others, 2009).

Physical solvents are used for high-pressure applications because at high pressures the capacity of CO_2 loading in physical solvents can far exceed that for loading into chemical solvents (Lurgi GmbH, 2010a). This is illustrated in Figure 7. The graph shows that CO_2 loading in the chemical solvents MEA and aMDEA® (activated MDEA) is higher than for Rectisol (methanol) at lower partial pressures but levels off as pressure increases. For physical solvents, the loading of CO_2 continues to increase linearly with increasing pressure. While Rectisol shows the highest CO_2 loadings on this graph, this occurs at temperatures that are at least 60°C lower than the other solvents. The energy cost of reducing syngas or natural gas to this temperature for treatment and other concerns such as the concentrations of H_2S, CO_2, and other constituents in the syngas influence the process selection decision. A good review of physical solvents for acid gas removal has recently been published (Burr and Lyddon, 2009).

There are three commercially available physical absorbent systems that have been marketed for capture of CO_2 from gasification fuel (syngas) and high-pressure natural gas sweetening:

- Selexol (UOP, LLC) [Genosorb® [Uhde GmbH] – dimethyl ethers of polyethylene glycol
- Rectisol (Lurgi GmbH, Linde AG) – chilled methanol
- Purisol (Lurgi GmbH) – N-methyl-2-pyrrolidone (NMP)

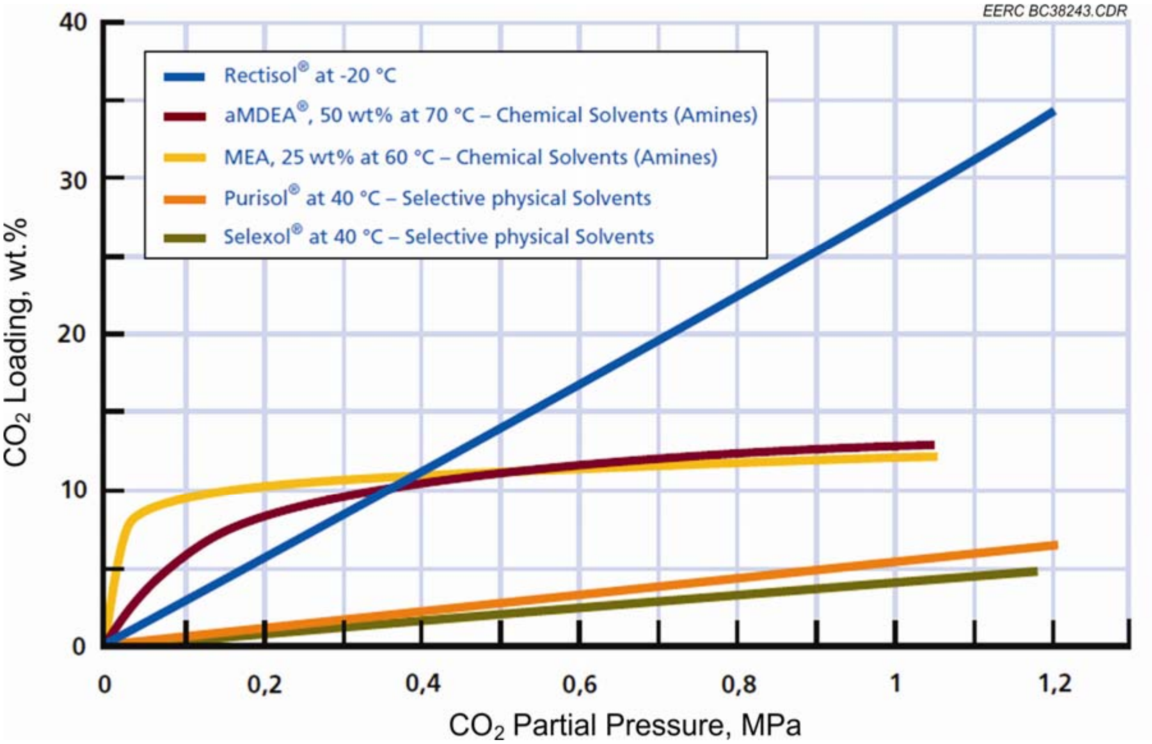

Figure 7. CO_2 loading capacity of different solvents (after Lurgi GmbH, 2010a).

Other physical solvents and physical solvent-based, high-pressure acid gas-scrubbing systems are marketed, including JEFFSOL-PC (Fluor solvent, marketed by Huntsman Chemicals), which is propylene carbonate, and Morphysorb (Uhde GmbH), which is composed of morpholine derivatives N-formylmorpholine (NFM) and N-acetylmorpholine (NAM).

Research also continues on the use and development of new physical solvents, including dimethyl carbonate and perfluorinated solvents. Mixtures of physical solvents and chemical solvents such as Shell Sulfinol (a mixture of diisopropanolamine and tetrahydrothiophene-1,1-dioxide) and UCARSOL™ LE Solvent 703 (LE-703, a Union Carbide Corporation-developed solvent made and marketed by Dow), and tertiary amines (e.g., aMDEA) are used in similar high-pressure acid gas removal applications.

Selexol

The Selexol technology from UOP, LLC, uses Dow Chemical's Selexol solvent, which is a mixture of dimethyl ethers of polyethylene glycol. The molecular formula is $CH_3O(CH_2CH_2O)_nCH_3$, where n is between 3 and 9 (Kuryachiy, 2007). A similar process, Genosorb, based on a similar chemical solvent mixture of dimethyl ethers of polyethylene glycol, is also available from Uhde GmbH.

The Selexol technology is a liquid physical solvent-based system for removing acid gases (H_2S, CO_2, and COS) from natural gas and syngas. It was developed over 35 years ago, and

55 commercial Selexol units had been put into service as of 2002 (Ciferno and others, 2006). It is applicable at feed pressures greater than 350 psia and acid gas concentrations of >5% by volume. It is generally regarded that a CO_2 capture efficiency of more than 85% can be achieved using the Selexol process (Metz and others, 2005). Selexol has a minimum operating temperature of 0°F (−18°C) (Bucklin and Schendel, 1984) and is typically operated at no more than 100°F (Ciferno and others, 2006).

Figure 8 shows the single-stage Selexol process, which is used when the concentration of H_2S in the gas stream is low. The gas is contacted with the Selexol solvent in the absorber tower. The acid gas-rich Selexol flows to the stripper tower, where it is heated to release the acid gases (primarily CO_2). The Selexol solvent is recycled back to the absorber tower (UOP, LLC, 2009b).

Selexol preferentially removes H_2S over CO_2, so when it is present with CO_2 as more than a low-concentration contaminant (such as in syngas), a two-stage Selexol process is used. In this embodiment, the H_2S is removed in an initial absorption step and CO_2 is removed during the second absorption. The process contains various recycle loops, heat exchangers, and flash separation drums. Breckenridge and others (2000) provide a good description of a two-stage Selexol process.

Advantages of the Selexol process include the fact that it has a higher capacity to absorb gases at high pressure than amines; less heat is required for CO_2 regeneration than is the case for amine processes; CO_2 is delivered at higher pressures than amine processes, meaning that less

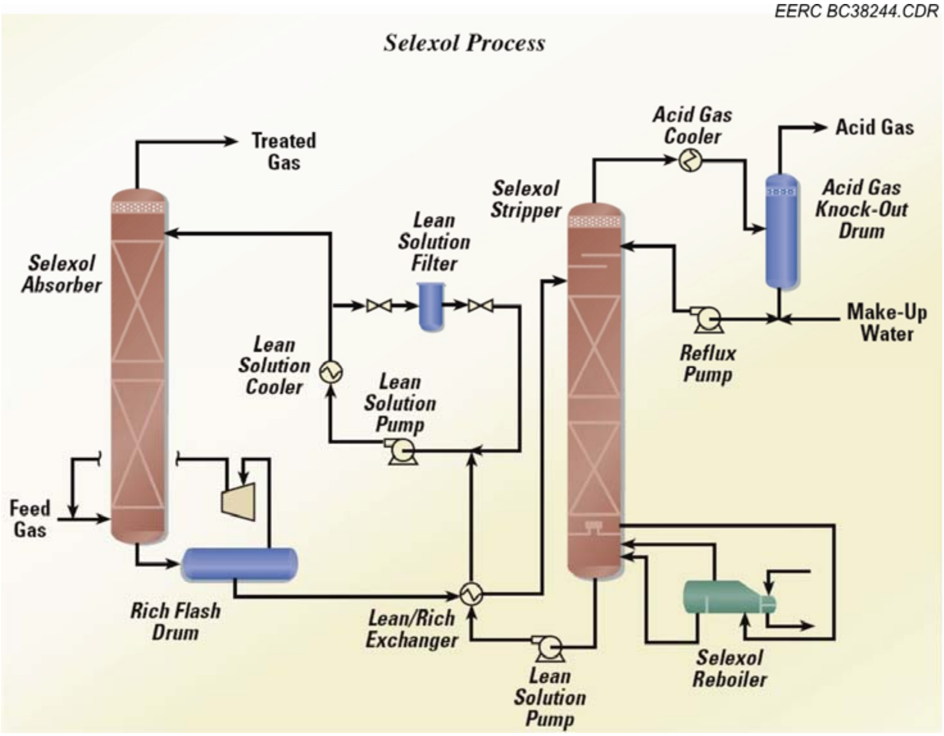

Figure 8. Selexol process schematic (taken from UOP, LLC, 2009b).

compression is required for transport to a geologic storage site; it does not form heat-stable salts during removal of H_2S and organic sulfur compounds; and simultaneous dehydration of the gas stream is provided (Clare and Valentine, 1984).

Disadvantages include the fact that the flue gas must be cooled to about 100°F and that CO_2 is regenerated by flashing, which requires recompression of the CO_2 stream for its transport (Ciferno and others, 2006).

Information about the Selexol process can be found in multiple sources (Breckenridge and others, 2000; Chen and Rubin, 2009; Chiesa and others, 2004; Doctor and others, 1996; U.S. Department of Energy National Energy Technology Laboratory, 2000; Pei, 2008; Probstein and Hicks, 2006; UOP, LLC, 2009b).

Rectisol

Rectisol technology is available from both Linde AG and Lurgi GmbH and uses methanol as the solvent. Lurgi provides the most complete description and process flow diagram for use in H_2S removal and CO_2 capture in syngas production (Lurgi GmbH, 2010a). Linde does not provide a process flow diagram showing CO_2 capture (Linde AG, 2010b). Prosernat IFP Group Technologies (2010) also supplies a methanol-based gas treatment process under the trade name Ifpexol® but appears not to be targeting it for CO_2 capture (Offshore Magazine, 2002).

The Rectisol process uses refrigerated methanol and usually operates at temperatures between −40° and −80°F (−40° and −62°C), although it can be operated at temperatures as low as −95° (−70.5°C) (Burr and Lyddon, 2009). Therefore, significant syngas cooling and reheating and a high electricity use demand for refrigeration come with the use of the Rectisol process. Great flexibility in process flow is possible for effecting a variety of separations, which may be useful for syngas separation into various components. A process flow diagram for the Rectisol process is given in Figure 9. All impurities and trace contaminants, such as CO_2 (<2 ppmv), COS, and H_2S (sulfur <0.1 ppmv), are removed in a single absorption process, thus generating an ultrapure product gas. In the single-stage Rectisol process for natural gas cleaning without CO_2 capture, N_2 stripping is used to separate the CO_2 from the methanol. When applied to syngas production, a two-stage Rectisol process is used for medium-pressure partial oxidation, with once-through Rectisol purification used for high-pressure partial oxidation (Hochgesand, 1970).

Advantages of using the Rectisol process include low power consumption; inexpensive, easily available solvent; and flexibility in process configuration. The high refrigeration costs hurt the economics compared to Selexol and Purisol for H_2S removal where CO_2 remains in the treated gas (i.e., where CO_2 capture is not required), but the high CO_2-loading capacity allows low solvent flow rates compared to other physical solvent processes and helps make the economics of the Rectisol process favorable for CO_2 capture applications (Ranke and Mohr, 1985).

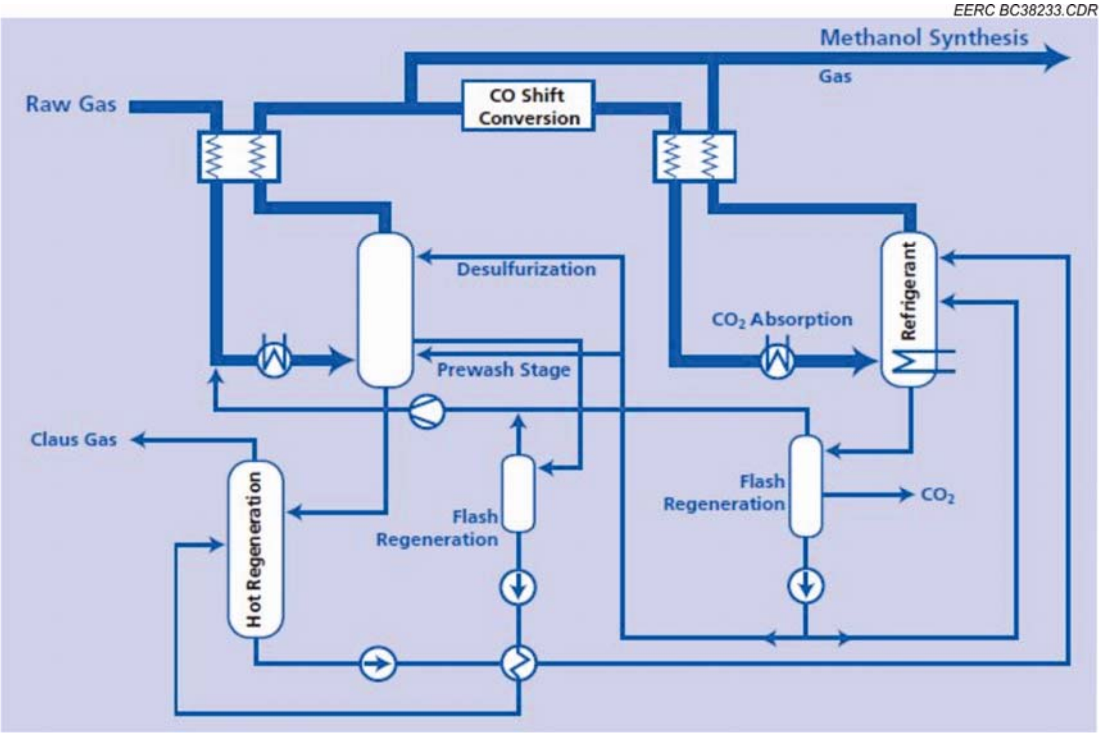

Figure 9. Process scheme for the Rectisol process (taken from Lurgi GmbH, 2010a).

Precombustion carbon capture using the Rectisol process is practiced at Dakota Gasification Company's Great Plains Synfuels Plant. The synfuels plant gasifies North Dakota lignite to produce synthetic natural gas and other products and captures up to 50% of the carbon originating in the coal as CO_2 (a large portion of the remaining carbon is not emitted as much remains in the synthetic natural gas and other organic carbon-based products produced by the facility). Dakota Gasification Company presents more information on carbon capture at its synfuels plant on its Web site (Dakota Gasification Company, 2010). Additional information about the Rectisol process can be found in Hochgesand (1970), Linde AG (2010b), and Lurgi GmbH (2010a).

Purisol

The Purisol process is marketed by Lurgi GmbH; however, it does not appear to be actively marketing Purisol at this time and does not provide a separate brochure for Purisol. The solvent used in the Purisol process is NMP. Purisol is used at temperatures between ambient and, with refrigeration, about 5°F (−15°C) (Burr and Lyddon, 2009).

Other Physical Solvents

JEFFSOL-PC

JEFFSOL-PC (aka Fluor solvent) is available from Huntsman Chemicals. It has been used in the Fluor Solvent Process licensed by Fluor since the late 1950s. It is applicable for CO_2

removal where little to no H_2S is present. The operating temperature for JEFFSOL-PC systems is limited to a range of 0°F (−18°C) to 149°F (65°C). It can be operated at intermediate pressures. More information on JEFFSOL-PC is available in Burr and Lyddon (2009), Huntsman Chemicals (2010), and Fluor Corporation (2010c).

Morphysorb

Morphysorb is a physical solvent for acid gas removal, marketed by Uhde GmbH. The solvent is a mixture of two morpholine derivatives, NFM and NAM, and it is highly selective for H_2S. It is not clear that it would be applicable for use in CO_2 capture. More detailed information is available on the Uhde GmbH Web site (Uhde GmbH, 2010).

Shell Sulfinol

This process is sometimes listed as a physical solvent process, but it is a combined physical and chemical solvent process. The physical solvent tetrahydrothiophene-1,1-dioxide (sulfolane) makes up 25% by volume of the mixture (Burlington Resources Canada Ltd., 2010). The chemical solvent diisopropanolamine (DIPA), a secondary amine, makes up approximately 35% to 45% by volume of the mixture (Burlington Resources Canada Ltd., 2010). The relative amounts of DIPA and sulfolane are adjusted for each application. It is used mainly in natural gas or syngas treatment where removal of both H_2S and CO_2 is important. It is used in a standard absorber–stripper arrangement. While it is not expected to gain widespread use for postcombustion CO_2 capture, there is reasonable potential for it to be used in precombustion applications (Burlington Resources Canada Ltd., 2010). More information on the Shell Sulfinol process is available online (Surface Production Facility, 2010a, b).

Physical Solvents under Development

Recent research reports on new physical solvents include a study on the use of DMC (dimethyl carbonate) by Gui and others (2010) and a report on the use of a perflorinated solvent (PP25 solvents, perfluoro-perhydro-benzyltetralin, C17F30) by Heintz and others (2006). The goal is to find a solvent with CO_2 capacity approaching that of refrigerated methanol (Rectisol) while operating at a much higher temperature. Gui and others (2010) conclude that DMC has a greater ability to dissolve CO_2 than propylene carbonate (JEFFSOL-PC) and methanol (Rectisol) when used at the same temperature and the solubility of CO_2 in DMC at room temperature (25°C, 78°F) is close to that in methanol at −10°C (14°F).

Commercially Available Chemical Absorption Technologies

While physical absorption technologies are often used in precombustion CO_2 capture and almost never considered for postcombustion CO_2 capture, chemical absorption technologies are used in both precombustion and postcombustion CO_2 capture. The original chemical absorbent technologies—those applied before the use of amines—were based on the use of caustic (hydroxide solutions) and hot carbonate solutions. The hot carbonate processes still have commercial viability in precombustion CO_2 capture. Regeneration of hydroxide solutions requires excessive amounts of energy, but these solutions do find use in mineralization applications.

The most readily available chemical absorption system for flue gas CO_2 capture is amine scrubbing with MEA. MEA is the most alkaline of the alkanolamines, a group of amines that includes DEA, diglycolamine (DGA), DIPA, and triethanolamine (TEA). Along with being the most alkaline MEA, it is the most strongly reactive of the alkanolamines listed, with respect to both kinetics (the speed of the reaction with CO_2) and thermodynamics (the strength of the chemical bond). This means it is easier to remove CO_2 from a flue gas with MEA than with the other alkanolamines, but it costs more energy to strip the CO_2 from solution in order to produce a purified CO_2 produce and regenerate the solvent for reuse.

Amine-based processes for acid gas removal can be and are commercially employed in both precombustion and postcombustion CO_2 capture applications, with MEA being the traditional solvent of choice for lower-pressure applications and aMDEA (MDEA solution with an activator, effectively a catalyst, added to it) the traditional solvent of choice for higher-pressure applications. Several other reactive chemical solvents and solutions are also being developed along with amines, hot carbonates, and caustics. These include ammonia (actually ammonium carbonate), metal carbonate solutions applied at lower temperatures, amino acid salts, and reactive ionic liquids. Catalysts, promoters, and chemicals to protect against oxidation of the chemical absorbent and corrosion of the equipment are often added to chemical absorbents. One area of significant development is the use of the enzyme carbonic anhydrase and synthetic compounds based on the reactive center of carbonic anhydrase as a catalyst.

A primary advantage expected from the selection of chemical absorbents other than MEA is reduction in the energy penalty of CO_2 capture. This expected reduction would come primarily from a reduction in the reboiler heat duty, where the decreased reboiler heat duty would come largely from a decrease in the thermodynamic strength of the CO_2–chemical absorbent bond and, thus, a reduction in the temperature of the steam and the amount of steam required to effect the desorption/stripping of the CO_2. Other factors that affect reboiler heat duty on a CO_2-mass-captured basis are the relative magnitude of CO_2 loading of lean and rich solutions and the concentration of the chemical absorbent in the absorbent mixture (Sakwattanapong and others, 2005; Oexmann and Kather, 2010; Ziaii and others, 2009).

Figure 10 illustrates the change in regeneration efficiency with respect to temperature for three chemical solvents: ammonia, DGA, and MEA. It is clear from the plot that much higher temperatures are required for regeneration (stripping) of MEA than for ammonia. DGA acts differently, with a gradual increase in regeneration efficiency with temperature over the full range.

The other improvements in energy efficiency of amine and other chemical solvent-based systems come from process improvements such as optimizing solution chemistry through adjustments in chemical concentration and the use of additives, the use of intercoolers in absorption towers, and better process integration, particularly with respect to heat exchange and heat recovery. Figure 11 illustrates the improvements made in lowering the thermal energy required for MEA and other amine-based systems over time.

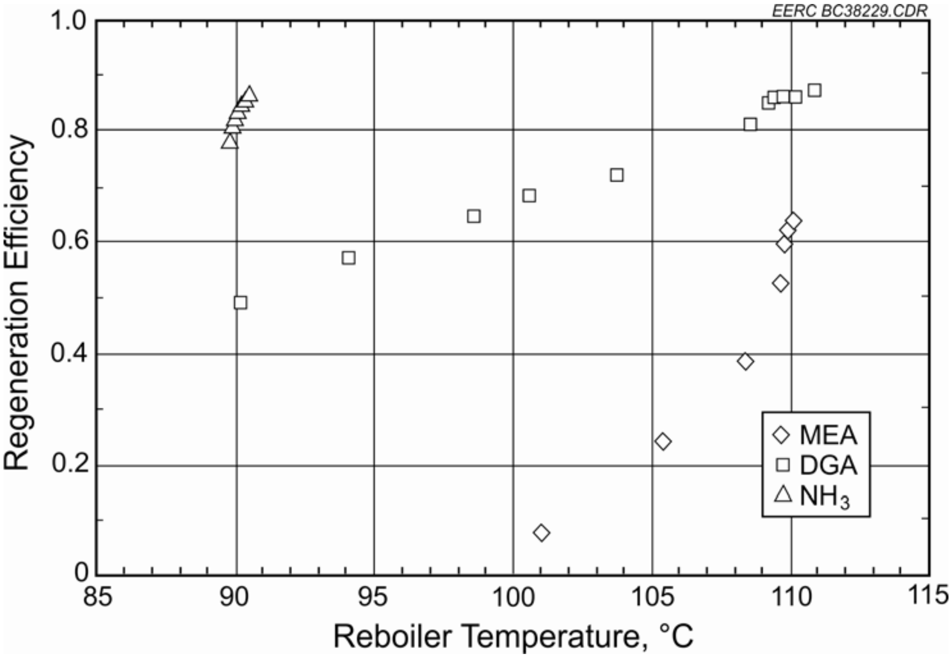

Figure 10. Regeneration efficiency in the desorber for a reboiler duty of 2.5–8.5 MW (after Pellegrini and others, 2010).

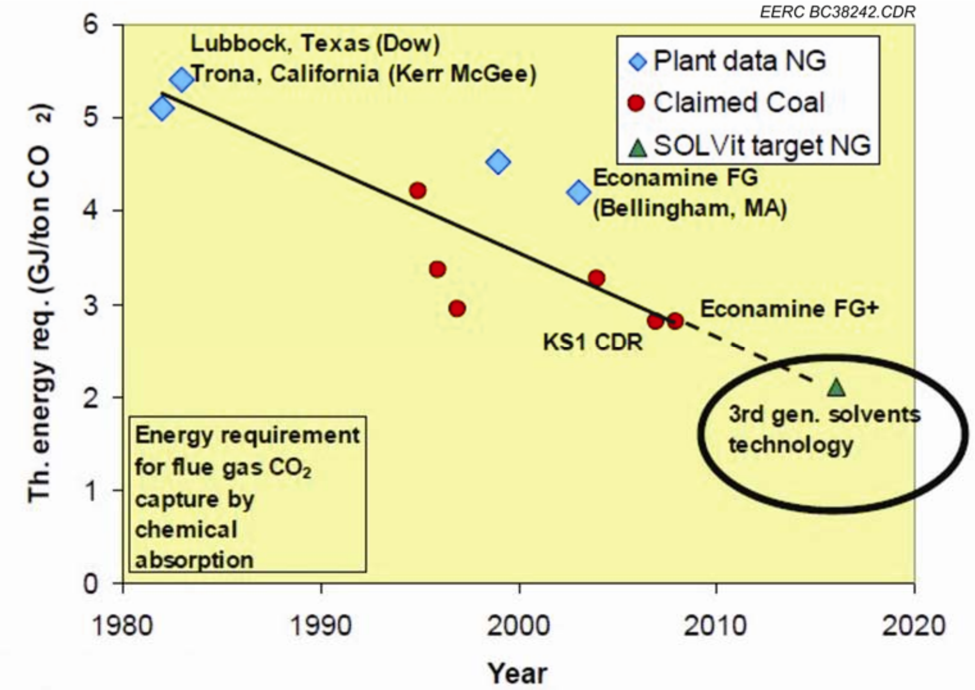

Figure 11. Decreasing thermal energy requirement for use of chemical solvents in commercial-scale CO_2 capture plants (the value shown for third-generation solvents illustrates the goal of the SOLVit development program) (taken from Nustad, 2009).

There are several commercially available chemical absorption systems that have been marketed and commercially applied for capture of CO_2:

- MEA-based processes
  - Fluor's Econamine FG℠ and Econamine FG Plus℠ processes – MEA
  - Lummus Technology/CB&I – Lummus MEA absorption process – MEA

- Kansi Mitsubishi Carbon Dioxide Recovery (KM CDR) Process – KS-1 proprietary (hindered secondary) amine

- Activated hot-potassium carbonate processes
  - Benfield process – UOP, LLC
  - CATACARB Process – Eickmeyer & Associates
  - Exxon Flexsorb® HP process
  - Giammarco-Vetrocoke's process

MEA-Based Processes

Several commercial facilities use MEA-based solvents to capture CO_2 from coal-, fuel oil-, and natural gas-derived flue gas streams for use in the food industry and other beneficial uses.

These plants have had capacities in the range of 100 to 1100 tons/day, which is significantly less than the 9000 tons/day produced by a 500-MW coal-fired plant. Commercial providers of MEA-based CO_2 capture technology include Fluor (Econamine FG and Econamine FG Plus) and Lummus Technology/CB&I. MEA is also widely used for H_2S scrubbing at oil refineries and in acid gas removal from raw natural gas.

A diagram of a generic system employing an MEA process for CO_2 capture was presented in Figure 6. Flue gas cooled to approximately 110°F and compressed to 17.5 psia by a centrifugal blower (to overcome the gas path pressure drop) enters the absorber base and flows upward countercurrent to the lean MEA solution. CO_2 is removed from the flue gas in the packed-bed absorber column through direct contact with the MEA solution. The CO_2-depleted flue gas is exhausted to the atmosphere. The CO_2-rich solution is heated in a heat exchanger (cross exchanger) and sent to the stripper unit where low-pressure steam (taken from the steam turbine crossover) is supplied to the reboiler for the thermal energy needed to liberate the absorbed CO_2. The CO_2 vapor is condensed, cooled, and sent to a multistage compressor where the CO_2 is compressed to a pressure of over 1200 psia. The CO_2-laden stream is dehydrated using glycol or molecular sieve processes. After drying, the CO_2 is ready for transport and sequestration.

The MEA process can achieve flue gas CO_2 recoveries of 80% to 95%, with product CO_2 purities over 99 vol% (Metz and others, 2005). However, the MEA process also requires a significant amount of power to operate pumps and blowers for gas and solvent circulation. The largest parasitic load to the power cycle is associated with the steam used for solvent regeneration. Solvent desorption heat consumption can be as high as 2.7 to 3.2 million Btu/ton CO_2 (Metz and others, 2005). Additional issues with the process are equipment corrosion;

solvent degradation caused by the presence of dissolved O_2 and other impurities; or reaction with SO_2, SO_3, and NO_x to produce nonregenerable, heat-stable salts. This requires SO_2 levels below 10 ppm, NO_2 levels below 20 ppm, and NO_x below 400 ppm. Solvent degradation and loss also occur during regeneration.

Fluor – Econamine FG and Econamine FG Plus Processes

The Econamine FG capture system was developed by the Fluor Corporation after it acquired the technology from Dow Chemical. It uses the primary amine MEA to capture CO_2 from flue gas in a regenerable reaction. The technology is applicable to gas streams containing 3% to 20% CO_2, with oxygen concentrations as high as 15% (by volume) (Fluor Corporation, 2010b). Proprietary corrosion and oxidation inhibitors are added to the MEA solvent to prevent degradation. The first generation of the system, known as Econamine FG used a 30% by weight MEA formulation. Econamine FG Plus technology is an advanced version of the Econamine FG technology, with significant improvements to the solvent and system. The improved solvent formulation provides a faster reaction rate and higher CO_2-loading capacity. The process improvements include a split-flow configuration, lean vapor compression, absorber intercooling, and integrated steam generation (Reddy and others, 2003). These are claimed to have reduced steam consumption by 20% and electricity consumption by 18% over the past 6 years (Broeils and Johnson, 2009). Figure 12 is a schematic of the Econamine FG Plus carbon capture process proceeded by a two-stage direct-contact cooler (DCC). Energy consumption for the Econamine FG Plus system is 1395 Btu/lb CO_2 captured.

Fluor's Econamine systems are commercially operated in 24 plants around the world, with 10 additional plants on order (Reddy and others, 2008). The Econamine process can be applied to power plants, steam reformers, and ammonia and MEA production plants. The Econamine FG process is installed at a natural gas-fired power plant in Bellingham, Massachusetts, where 365 short tons per day of CO_2 is recovered. Fluor and E.ON Energy plan to conduct a demonstration of CO_2 capture at a supercritical coal-fired plant using the Econamine FG Plus system. The process has also been selected for a DOE-supported Clean Coal Power Initiative (CCPI 3) project in which NRG Energy will evaluate the economine FG Plus process at the W.A. Parish plant (U.S. Department of Energy National Energy Technology Laboratory, 2010f). The goal is to capture up to 400,000 metric tons per year (1095 metric tons/day) of CO_2. Detailed information on the Fluor Econamine FG and FG Plus processes is available from the Fluor Corporation (2010a).

Lummus MEA Absorption Process

The Lummus MEA absorption process, also known as the Kerr-McGee/ABB Lummus Crest process (Barchas and Davis, 1992), has been used to recover CO_2 from coke and coal-fired boilers, delivering CO_2 for soda ash and liquid CO_2 preparations. It uses a 15%–20% by weight aqueous MEA solution with corrosion and oxidation inhibitors. The largest-capacity plant using this process produces 800 tons of CO_2 per day while utilizing two parallel trains (Arnold and others, 1982). The process has been used for production of both food- and chemical-grade CO_2 for many years. Typically, about 75% to 90% of the CO_2 in the flue gas is captured using this

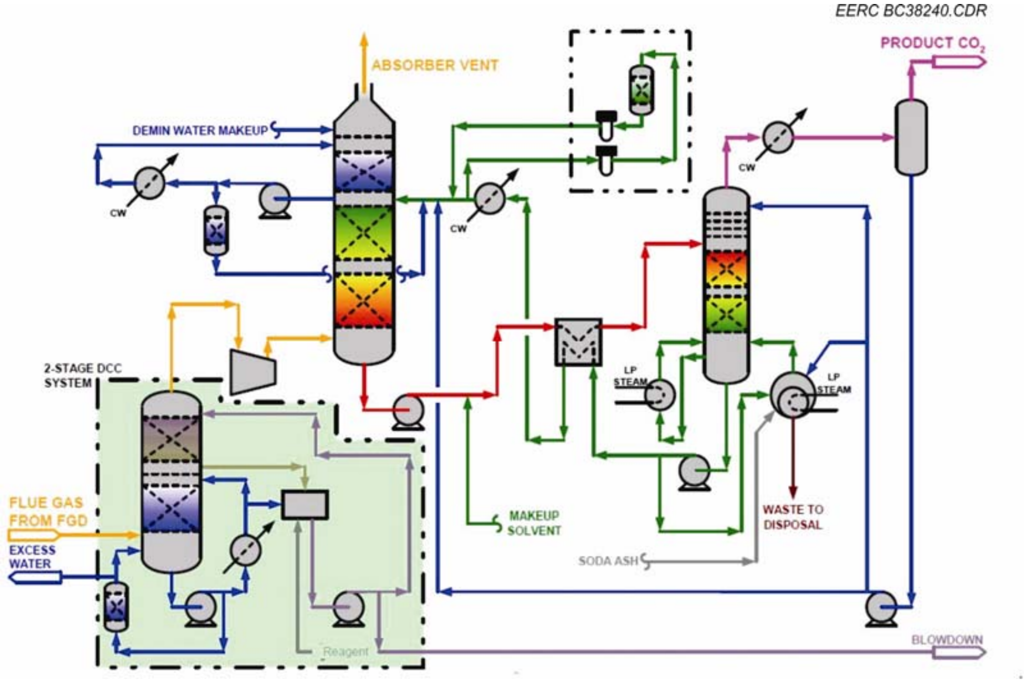

Figure 12. The Fluor Econamine FG Plus for coal-fired power plant flue gas (taken from Broeils and Johnson, 2009).

technology, producing a nearly pure (>99%) CO_2 product stream (Rubin and Rao, 2002). The process employs the same configuration as the other standard absorber–stripper processes.

The Lummus scrubber system is installed at the Shady Point cogeneration plant in Panama, Oklahoma. The 320-MWe-net-output cogeneration plant is a circulating fluidized-bed combustion-based facility that fires hard coal. The plant consumes roughly 800,000 metric tons of coal each year. Approximately 5% of the flue gas is diverted and transported to the adjacent CO_2 capture plant by centrifugal blowers. About 65,000 lb/hr of 75-psig steam is used in the capture facility to extract 200 tons per day of food-grade CO_2 from the plant's flue gas (International Energy Agency, 2009a).

Another demonstration project using the Lummus scrubber at commercial scale is the Warrior Run power plant in Cumberland, Maryland, a 180-MW cogeneration plant based on circulating fluidized-bed combustion technology (International Energy Agency, 2009b). Nearly 150 tons of liquid CO_2 per day is sold for fire extinguishers and food cooling. About 4 MW of the gross electrical output is used to operate the capture plant (Page and others, 2009).

Mitsubishi Heavy Industries (MHI) – KM CDR Process

The KM CDR process offered by MHI is an intercooled absorber–thermal desorption stripper (steam fed reboiler) CO_2 capture process that uses the sterically hindered amine KS-1. The process flow diagram is very similar to that for any other absorber–stripper process. The hindered amine chemical absorbent KS-1 is reported to have a molecular structure that is tailored to enhance its reactivity toward CO_2. Reported benefits of the process include low regeneration heat requirements, low solvent degradation without the use of additives or inhibitors, and low amine losses (Jansen and others, 2007).

The history and capacity of MHI's research, demonstration, and commercial plants for CO_2 capture from natural gas and coal are shown in Figure 13. MHI has a significant and aggressive history with development and demonstration of large-scale CO_2 capture plants. The company currently offers the KM CDR at full commercial scale, with performance guarantees for natural gas-fired power plants. MHI expects to be able to offer similar full commercial-scale KM CDR plants with performance guarantees once they gain sufficient operational experience with large-scale facilities run on coal-derived flue gas (Iijima and others, 2010). Operation of the planned facilities listed in Figure 13 would likely provide the desired operational experience necessary to allow MHI to provide performance guarantees. More detailed information on MHI's KM CDR process is available from numerous sources (Iijima and others, 2010; Kamijo and others, 2004; Mitsubishi Heavy Industries, 2006, 2010; Mimura and others, 2000; Ronald, 2008; Ohishi and others, 2006; Yagi and others, 2006).

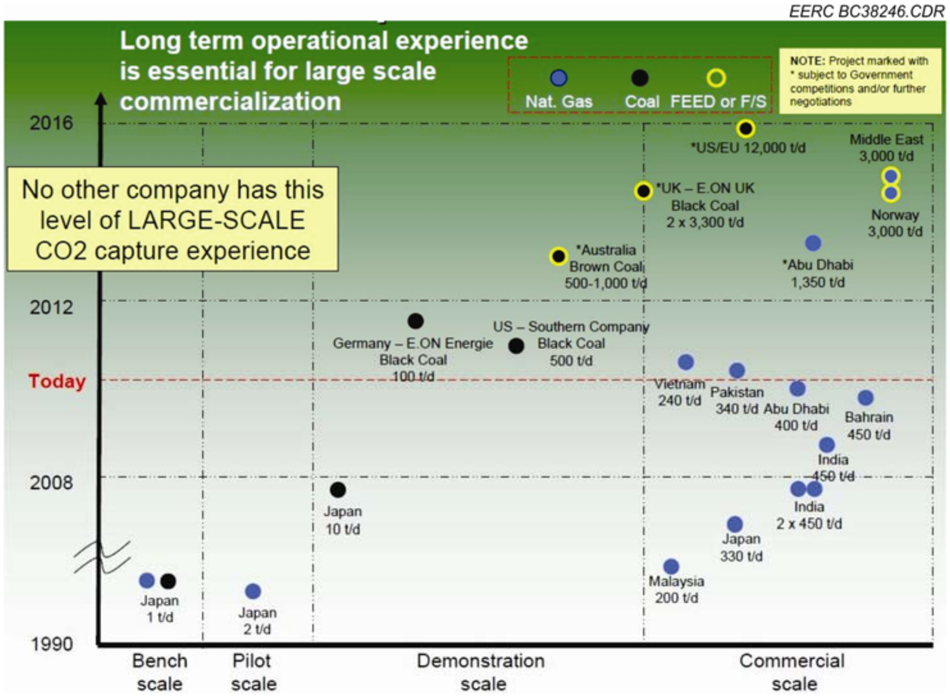

Figure 13. MHI CO_2 Capture reference plants (the yellow-circled points represent planned facilities) (taken from Iijima and others, 2010).

Activated Hot-Potassium Carbonate Processes

Commercially available activated hot-potassium carbonate (AHPC) processes employ aqueous potassium carbonate (K_2CO_3) as the reactive solvent with an activator (catalyst) for the chemical absorption of CO_2 in an absorber operated at a relatively high temperature and high pressure. The processes are applicable to precombustion capture. To improve CO_2 absorption mass transfer and to inhibit corrosion, proprietary activators and inhibitors are added. The most widely licensed of the AHPC systems are the Benfield process, with over 675 units worldwide, licensed by UOP, LLC (2010), and the CATACARB process, with over 100 units licensed as of 1992 by Eickmeyer & Associates (CATACARB, 2010). Other commercial AHPC processes are the Exxon Flexsorb HP process, which uses a hindered-amine activator, and Giammarco-Vetrocoke's process, which uses an organic activator.

The Benfield and CATACARB processes are commercially offered for applications at a minimum CO_2 partial pressure of 210 to 345 kPa (1 atm = 101.325 kPa) and an optimum operating pressure of 700 kPa. Solvent regeneration is accomplished through pressure reduction and heating. Literature discussing the Benfield process indicates that recent process improvements (new activator and improved column internals) have resulted in reduced CO_2 concentrations in the treated gas and reductions in regeneration heat and solution pumping requirements) (Chapel and others, 1999).

The absorption and regeneration of acid gases in the Benfield process are based on the following reactions:

$$K_2CO_3 + CO_2 + H_2O \rightarrow 2KHCO_3 \qquad \text{[Eq. 1]}$$

$$K_2CO_3 + H_2S \rightarrow KHS + KHCO_3 \qquad \text{[Eq. 2]}$$

The absorption and regeneration of acid gases are conducted in a similar way to that of the conventional amine or carbonate processes. The gas to be treated is fed to the bottom of the absorber and flows countercurrently to the absorbing liquid supplied at the top of the absorber. Acid gases are then absorbed by the absorbing liquid. The liquid that has absorbed the acid gases is preheated and then supplied to the top of the regenerator where the acid gases are stripped by steam for the regeneration of the liquid. The regenerated liquid is cooled and recirculated to the absorber. The process is shown in Figure 14.

Pilot- and Demonstration-Scale Chemical Absorption Technologies

Other chemical solvent processes have been demonstrated at the pilot scale or are in the process of moving to pilot-scale demonstration. They are discussed in the following subsections.

Aker Clean Carbon

Aker Clean Carbon is involved in work on chemical solvent carbon capture. Its activities include the following:

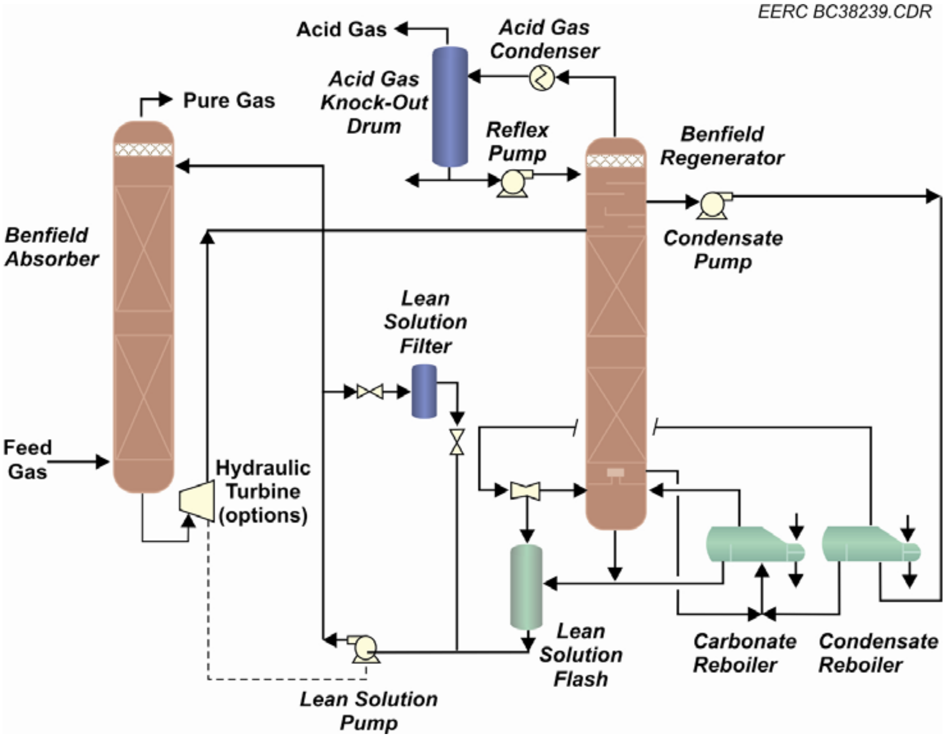

Figure 14. Benfield process (taken from UOP, LLC, 2009a).

- Development of new solvents through involvement with the CASTOR project and SOLVit.

- Construction and operation of a mobile test unit (MTU) for testing solvent performance on real flue gas (Figure 15).

- Leading a 12-member consortium group to develop JustCatch^{TM} technology, which included study and front-end engineering design for a full-scale amine-based capture plant.

- Selection for construction and management of a flexible amine pilot facility (capacity: 78,000 tons of CO_2 per year) in Mongstad, Norway.

- Participation in the European CO_2 Technology Centre at Mongstad, Norway.

- Full-scale plant project at Kårstø.

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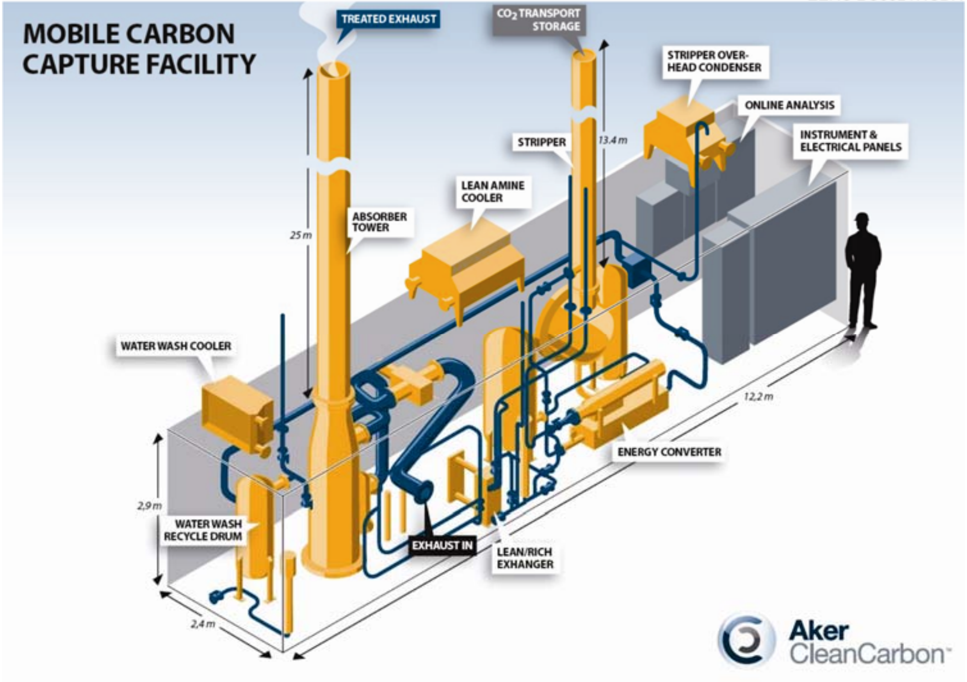

Figure 15. Aker Clean Carbon’s MTU for testing chemical solvent-based CO_2 capture (taken from Aker Solutions, 2010).

- Competing for a United Kingdom carbon capture and storage (CCS) coal project (Scotland).

ALSTOM – Chilled Ammonia Process (CAP)

ALSTOM’s CAP is a solvent-based regenerable process that utilizes the low-temperature, low-energy reaction of an aqueous ammonium carbonate solution with CO_2 to form ammonium bicarbonate. A schematic of CAP, showing the flue gas-cooling system, absorption system, and regeneration system, is shown in Figure 16. The process captures CO_2 from flue gas by directly contacting it with a CO_2-lean solution at temperatures below 20°C (40°F). In the primary absorption reaction, ammonium carbonate reacts with CO_2 in the flue gas to form ammonium bicarbonate, which precipitates as a solid. This solid is concentrated and sent to the regeneration unit where the chemical reaction is reversed through the application of heat. CO_2 released by the regeneration reaction pressurizes the system. The regenerated lean solution is returned to the absorber where it is reused to capture CO_2 once again. The process was designed for a CO_2 removal efficiency of 90% (Kozak and others, 2009).

Absorption and regeneration are performed under optimal NH_3/CO_2 ratios, meaning that appreciable free ammonia does not exist under the operating conditions, thus minimizing potential for ammonia slip (loss to the atmosphere). The low-temperature absorption results in high solubility of CO_2 in the aqueous alkaline solution. CAP can be retrofitted onto existing

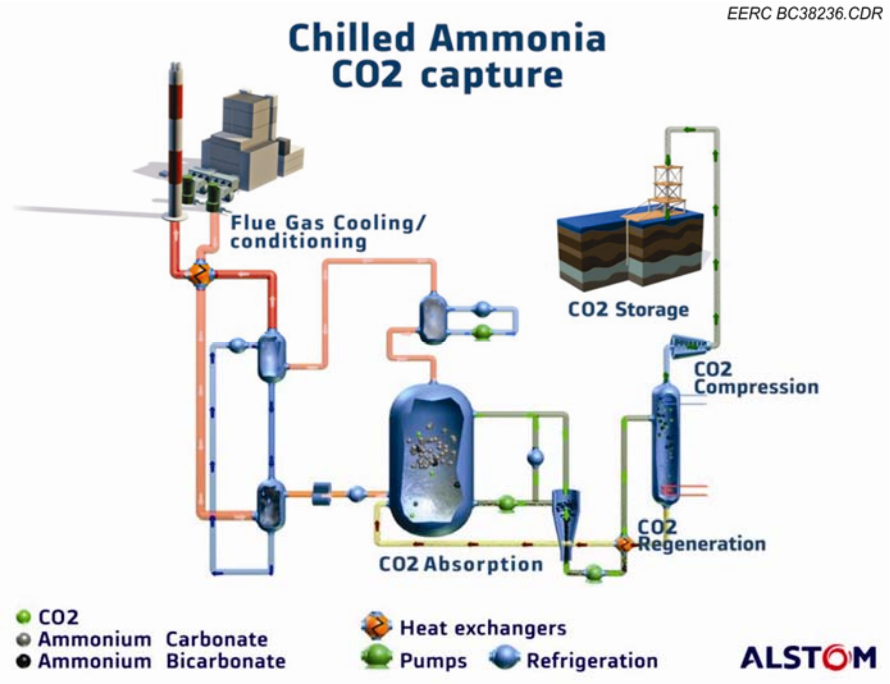

Figure 16. ALSTOM CAP (taken from ALSTOM Power, 2010a).

coal-fired power plants. The use of low-reaction-energy ammonium carbonate reduces the steam input required to release the CO_2. During regeneration, the scrubber operates at a pressure of 300 psi. This compares to the 15 psi at which amine systems produce CO_2. This differential offers significant savings in compression energy for CAP (Blankinship, 2008a).

Additional energy required for CAP, including auxiliary power and low-pressure steam for the stripper, is much lower than the energy required by a traditional amine process. ALSTOM believes CAP can reduce a power plant's parasitic load for carbon capture to about 15% to 18% from the approximately 30% parasitic load of a traditional MEA process (Blankinship, 2008a). Other CAP advantages include a high CO_2 load capacity for the solution (0.1 to 0.2 lb CO_2 per lb solution), low heat of reaction (HR), low cost of reagent, no degradation during absorption–regeneration, and tolerance to oxygen and contaminants in the flue gas (Rhudy and Black, 2007).

Because the regeneration heat required (approximately 400–700 Btu/lb CO_2 captured) (Rhudy, 2006) is so much lower than that needed for MEA-based capture the system will have much lower direct impact on an existing plant's steam cycle – a significant advantage for retrofit applications. The large refrigeration system needed to chill the flue gas and keep absorber operating temperature below 50°F will consume electricity, but the electricity used should not exceed that which can be produced by the low-pressure steam that would have been used to regenerate MEA.

A baseline study of the auxiliary load and cost of a full-scale CO_2 capture process found that retrofitting a 462-MW supercritical pc-fired boiler operating at 40.5% net thermal efficiency would result in only small performance penalties (Peltier, 2008). CO_2 avoided cost was $19.7/ton

(Rhudy and Black, 2007). A comparison of a theoretical power plant with CAP installed to one without CO_2 capture is shown in Table 1 (Rhudy and Black, 2007).

ALSTOM has performed several projects in the course of preparing CAP for market. These include, but are not limited to, the following three U.S.-based projects designed to provide stepwise scale-up and demonstration to full commercial scale for pc-fired power plants:

- ALSTOM and the Electric Power Research Institute (EPRI) operated their first coal-fired power plant flue gas demonstration project on a 1.7-MW (electric)-equivalent slipstream at We Energies' Pleasant Prairie plant in Wisconsin. This test demonstrated 90% CO_2 capture; ammonia loss in the treated flue gas of <10 ppmv and the production of high-quality CO_2 (>99.5% purity). The pilot plant was operated for >7000 hours and captured CO_2 at a rate of over 35 tonnes/day (Kozak and others, 2010).

- Currently, ALSTOM is involved in the second-phase scale-up demonstration of CAP at American Electric Power's (AEP's) Mountaineer plant in New Haven, West Virginia. This phase will capture about 90% of the CO_2 from flue gas equivalent to 30 MW of the coal-fired power plant's output. This is equivalent to over 250 tonnes/day. AEP and Battelle Research Institute will sequester the captured CO_2 at a nearby site.

- ALSTOM's third step in preparing CAP for commercial use will be applying the process at commercial scale at AEP's Northeastern Station at Oologah, Oklahoma. CO_2 will be captured from a full-scale pc plant generating 300 MW of electricity. The approximately 1.5 million tons of CO_2 per year that is captured will be used nearby for EOR.

Table 1. Performance Penalties of a Chilled Ammonia CO_2 Separation System (Rhudy and Black, 2007)

Parameter	Supercritical pc Without CO_2 Removal	Same Unit with CO_2 Removal
Illinois No. 6 Coal Feed Rate, lb/hr	333,542	333,542
Coal Heating Value, Btu/lb, HHV[a]	11,666	11, 666
Boiler Heat Input, MMBtu	3891	3891
Low-Pressure Steam Extracted for Reboiler, lb/hr	0	179,500
Steam Turbine Power, kW	498,319	484,995
Total Auxiliary Power, kW	29,050	53,950
Net Power Output, kW	462,058	421,171
Net Efficiency, %, HHV	40.5	37.0
CO_2 Avoided Cost, \$/ton CO_2	Base	19.7

[a] Higher heating value.

Additional information on CAP can be found on ALSTOM Power's Web site (ALSTOM Power, 2010a).

ALSTOM – Advanced Amine Process (AAP)

In addition to its work on CAP, ALSTOM is involved in development, pilot-scale work, and front-end engineering and design of an advanced amine process in partnership with Dow Chemical as the amine supplier. This has progressed to the selection of the Dow UCARSOL FGC Solvent 3000 as the amine and operation of a demonstration project that captures CO_2 from the flue gas of a coal-fired boiler at the Dow-owned chemical facility in South Charleston, West Virginia. The pilot project has been reported to have successfully operated for over 4500 hours, captured 90% of the CO_2 in the flue gas stream, and produced a CO_2 containing at least 99.5% CO_2. The pilot project is scheduled to run until Fall 2011 (Electric Light and Power, 2010).

ALSTOM has also announced two other advanced amine process projects:

- An industrial demonstration facility to capture carbon dioxide at the Le Havre coal-fired electric power plant in France, which is scheduled for start-up by 2012. The project program includes execution, testing, evaluation, and validation phases of the CO_2 capture unit at the production site. It is partially funded by the French governmental body ADEME (The French Environment and Energy Management Agency) (ALSTOM Power, 2010b).
- Study and engineering project for a 20-MW_{th} lignite-powered facility at PGE Belchatow, Poland (Kozak and others, 2010).

Cansolv CO_2 Capture Process

Cansolv Technologies Inc. (CTI) offers two different amine-based systems that are capable of capturing CO_2. One is a fairly standard absorber–stripper arrangement designed for CO_2 capture alone. The other is an integrated SO_2 control and CO_2 capture system, shown schematically in Figure 17. CTI uses patented amine solutions DC-103 and DC-103B. Project-specific issues determine which solution will be used. DC-103 has a lower regeneration energy requirement (i.e., the parasitic energy load is lower) and slower kinetics (i.e., a larger absorption tower is needed) than DC-103B (Shaw, 2009). Table 2 is a list of pilot projects in which CO_2 capture was evaluated for the Cansolv process.

The Cansolv SO_2–CO_2 integrated capture process has been selected for two projects:

- The RWE Power carbon dioxide capture pilot project at Aberthaw power station in South Wales, United Kingdom, will be a 3-MW-equivalent, with 50 tonnes per day of CO_2 captured from a slipstream from the pc-fired power plant. The pilot plant will be operated for 2 years. Construction is expected to start in 2010, with commissioning expected in 2011.

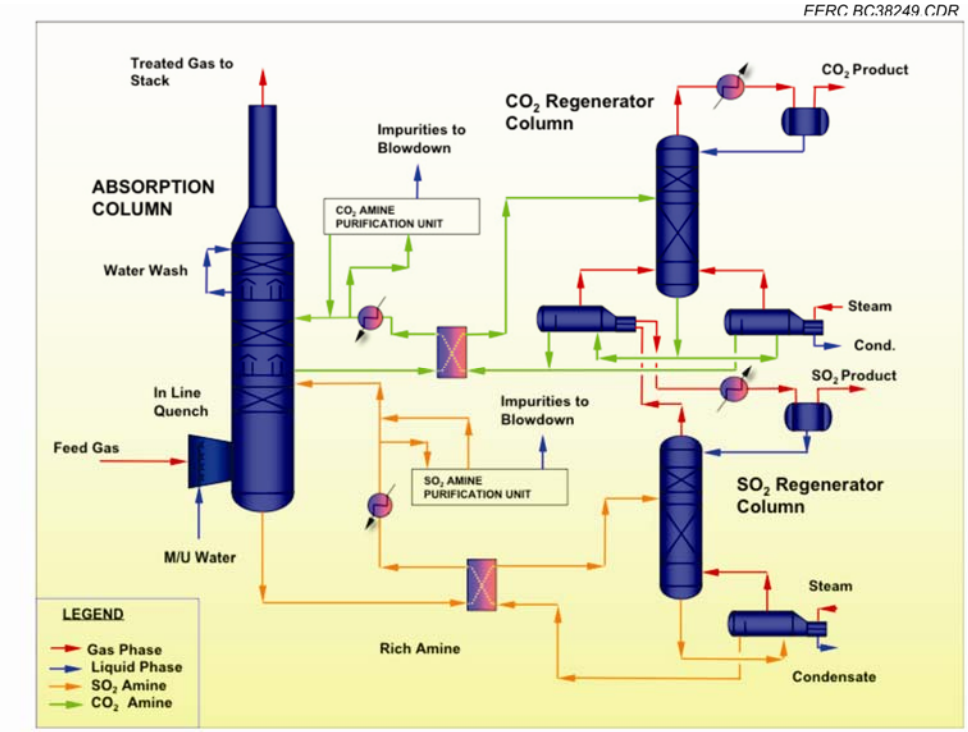

Figure 17. Simplified process flow diagram of the Cansolv SO_2–CO_2 integrated capture process (taken from Just and Shaw, 2008).

Table 2. List of Cansolv CO_2 Pilot Projects Through Early 2008 (Shaw, 2009)

Application	Date	Site	CO_2 in the Gas, vol%	Removal, %
Natural Gas-Fired Boiler	March–June 2004	Paprican, Montreal, Canada	8	75
Coal-Fired Boiler	November 2004	Pulp Mill Boiler, USA	11.5	65
Coal-Fired Power Plant	July–Sept 2006	SaskPower, Poplar River, Canada	12	90
Blast Furnace	April 2007–2008	Japan	22	90
Natural Gas-Fired Boiler	May–Sept 2007	Shell-Statoil, Norway	4.5	85
Cement Kiln	Jan–Feb 2008	North America	20	90 and 45

- For SaskPower's Boundary Dam integrated CCS demonstration project, SNC Lavalin will serve as the engineering and construction firm. The SNC Lavalin–Cansolv proposal was selected as the preferred of the three proposals which had been short-listed by SaskPower in February 2009. Powerspan and Fluor were the two other candidate capture technology providers. SaskPower will make a final decision on whether to proceed with the Boundary Dam CCS project later in 2010. The project will be supported by the Canadian government. The CO_2 will be sold for use in EOR (Canada Views, 2010).

HTC Purenergy Carbon Capture System

HTC Purenergy Inc. is a small, publicly traded company located in Regina, Saskatchewan, Canada. Doosan Babcock jointly with its parent company, Doosan Heavy Industries and Construction, holds an exclusive global technology licensing agreement with HTC Purenergy for its postcombustion carbon capture (PCCC) technology (Doosan Babcock, 2008, 2010). The global technology licensing agreement includes the right for Doosan Babcock to utilize products and technologies developed by HTC Purenergy and the University of Regina Green House Gas Technology Centre in Saskatchewan, Canada. HTC Purenergy has a close relationship with the University of Regina and uses its Green House Gas Technology Centre facilities, scientists, and engineers for research and development of its CO_2 capture technology.

According to the HTC Web site (HTC Purenergy Inc., 2009) and press releases, HTC Purenergy currently offers the Purenergy CCS system for postcombustion flue gas capture of CO_2. The Purenergy system is advertised to be preengineered, prebuilt, and modular using technologies developed and validated for over 15 years at the University of Regina. A single modular process train is stated to be capable of capturing up to 3000 tons per day of CO_2. An artist's rendering of the system and is given in Figure 18.

The process falls into the category of a chemical absorbent-based, absorber–stripper-based CO_2 capture system with thermal regeneration of the solvent. Solvent selection, modular system design, and process optimization appear to be the focus in preparing the process for deployment. The claimed benefits of the advanced amine-scrubbing technology include:

- High efficiency with a reduction of energy consumption.
- Unique formulated solvents.
- Less corrosive solvents.
- Lower cooling water requirements.
- Reduced operating cost.

To date, there have been no large-scale pilot projects performed based on the use of this technology, but Basin Electric Power Cooperative has selected it for the planned 120-MW-equivalent slipstream carbon dioxide capture plant at its Antelope Valley Station (AVS) located near Beulah, North Dakota (Basin Electric Power Cooperative, 2009).

Linde AG with BASF Solvents

In 2007, Linde AG and BASF signed a joint development agreement for design, construction, testing, and commercialization of advanced PCCC technology. This included a detailed study for selection of a chemical absorbent solution that started with the screening of approximately 400 substances. The screening procedure, illustrated in Figure 19 narrowed the list to approximately 15 substances that were tested in a miniplant and left two that will be tested

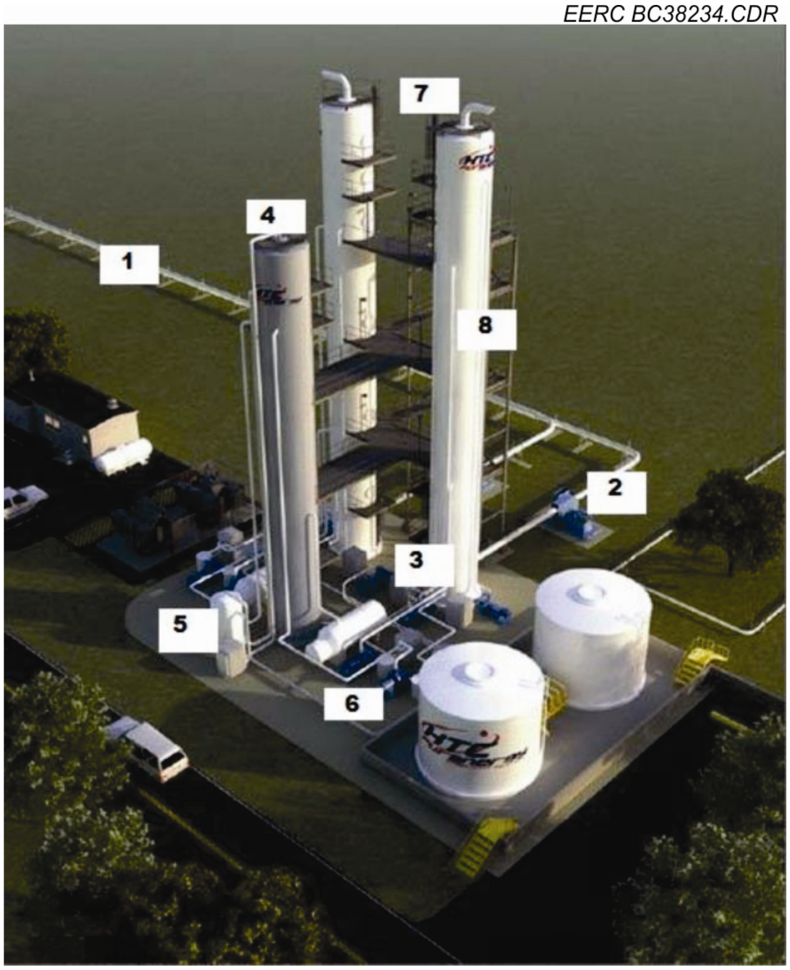

Figure 18. HTC Purenergy CCS system (The numbers represent process description statements available on the company Web site) (taken from HTC Purenergy Inc., 2009).

in the approximately 7.2-tonne/day CO_2 pilot plant. The pilot plant (Figure 20) has been constructed at RWE Power's lignite-fired power plant in Niederaussem, Germany, and can process 60 mcf/hr of flue gas. Testing began in June 2009 with a target plant efficiency loss of less than 10% and a CO_2 avoidance cost of less than €30/tonne CO_2 (Krishnamurthy and Holling, 2010).

Powerspan

Powerspan Ammonia-Based ECO_2™ Process

Powerspan moved from use of aqueous ammonia to a proprietary solvent during the course of operating its pilot project at FirstEnergy Generation Corporation's R.E. Burger plant near Shadyside, Ohio. The change in solvent occurred sometime in 2009 but was not made public until a platform presentation at the 9th Annual CCS Conference in Pittsburgh, Pennsylvania, in

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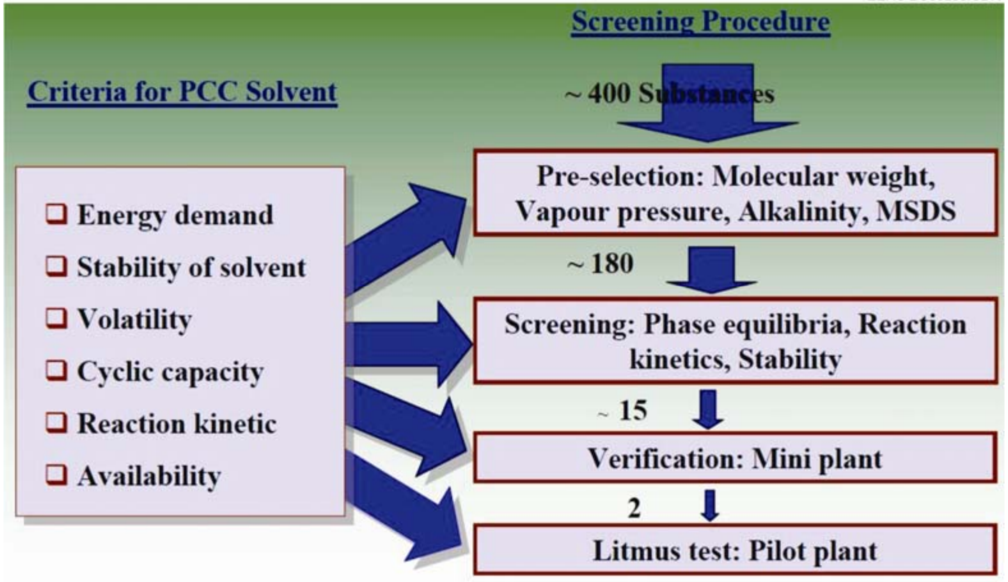

Screening Procedure

Criteria for PCC Solvent

- ❑ Energy demand
- ❑ Stability of solvent
- ❑ Volatility
- ❑ Cyclic capacity
- ❑ Reaction kinetic
- ❑ Availability

~ 400 Substances

Pre-selection: Molecular weight, Vapour pressure, Alkalinity, MSDS

~ 180

Screening: Phase equilibria, Reaction kinetics, Stability

~ 15

Verification: Mini plant

2

Litmus test: Pilot plant

Figure 19. BASF screening of substances for use in chemical absorption CO_2 capture (taken from Krishnamurthy and Holling, 2010).

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Figure 20. Postcombustion CO_2 capture pilot plant in Niederaussem, Germany (taken from Krishnamurthy and Holling, 2010).

May 2010 (Boyle and Andes, 2010). Because Powerspan is no longer using the aqueous ammonia process, the details of that process will not be covered here except to say it differed from ALSTOM's CAP, most notably in that the flue gas was not cooled (as in CAP) and it was integrated with Powerspan's ECO process for SO_x and NO_x removal.

Powerspan Proprietary Solvent-Based ECO_2 Process

Powerspan's proprietary solvent ECO_2 process appears to be a fairly standard thermal swing absorption–regeneration process (Figure 21). The CO_2 scrubber is a packed absorber tower. The flue gas is accepted by the CO_2 scrubber at or slightly cooled from the outlet conditions of an SO_2 scrubber. CO_2 is absorbed into the solvent as the flue gas passes upward through the absorber and the solvent flows downward (countercurrent flow). The resulting CO_2-rich solvent exits the CO_2 scrubber, passes through a cross heat exchanger, and enters the top of a regenerator (stripper).

Powerspan reports (Boyle and Andes, 2010) that its pilot facility work demonstrated advantages of the ECO_2 process that include:

- Low energy of regeneration (i.e., less than 1000 Btu/lb of CO_2).
- High solvent stability (no thermal or oxidative breakdown at operating conditions).
- Low vapor pressure for the solvent at absorber operating conditions (avoiding the need to water-wash the flue gas prior to release from the CO_2 scrubber).

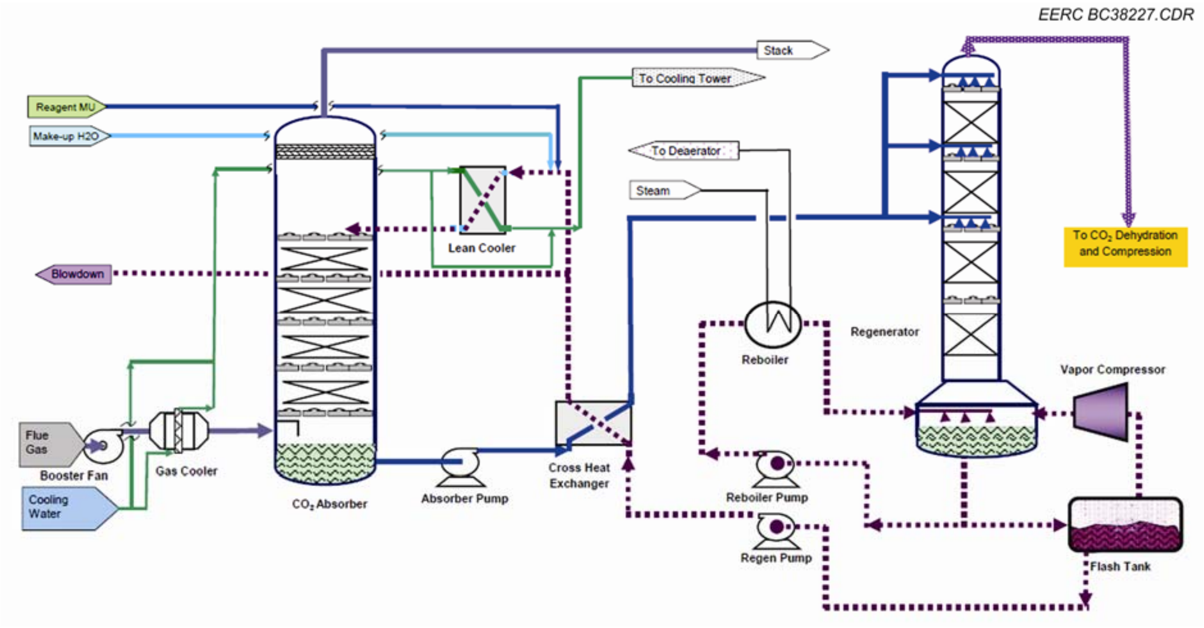

Figure 21. Powerspan's proprietary solvent ECO_2 process (taken from Boyle and Andes, 2010).

It also claims that the proprietary-solvent ECO_2 process is capable of removing other acid gas contaminants (e.g., SO_2, SO_3, NO_2, and HCl) captured from the flue gas and into the solvent at a low cost, thus allowing the process to function without a polishing scrubber (in many applications). This process has not been described publicly.

WorleyParsons was hired to confirm the pilot study results and perform a modeling and economic study on the process. It found that the Powerspan proprietary solvent-based ECO_2 process would decrease the net output of the power plant from the CO_2 capture process by 30% as a result of steam extraction and the increased auxiliary load. This is a 9.97% reduction in plant net efficiency for the subcritical steam cycle studied (Boyle and Andes, 2010).

An all-in capital cost estimate for a proprietary-solvent ECO_2 system for a 220-MW net reference plant was \$304 million. The total estimated cost of captured CO_2 was \$36.61/ton (valuing the lost net generating power at \$50/MWh and assuming 40 ppm of SO_2 in the inlet gas stream) (Boyle and Andes, 2010).

Sargas Carbonate Process

Sargas AS, a Norwegian start-up company based in Oslo, has developed a pressurized combustion, combined-cycle power generation system with CO_2 capture. Two versions of this power plant were designed, one for natural gas (pressurized natural gas combustion [PNGC], 100 MW) and one for coal (pressurized fluidized-bed combustion [PFBC], 400 MW). The system is claimed to be a postcombustion, preexpansion design. This process differs considerably from the other postcombustion technologies discussed because it is an integrated power plant with a postcombustion capture process, not a CO_2 capture process that can be used on an existing plant.

The process, illustrated schematically in Figure 22, begins with compression of the air prior to sending it to a pressurized boiler. In the boiler, either natural gas or coal is combusted with the air. The generated steam is fed to a conventional steam turbine where it is expanded, then condensed and returned to the boiler. The combustion is kept to about 2% excess of oxygen. The flue gas from the boiler at 850°C is directed through the heat exchanger to cool down to 70°C. The cool flue gas enters an absorption column where it reacts with potassium carbonate to remove CO_2. A modified Benfield process (20–40 wt% of potassium carbonate) is used. The decarbonized flue gas is sent back to the heat exchanger to reheat to 840°C. Then the flue gas is fed to a gas turbine where it is expanded to produce power. The steam turbine generates about 80% of the electricity, and the gas turbine generates about 20% (Bryngelsson and Westermark, 2005).

Net efficiency for a 100-MW natural gas power plant is claimed to be 40% on a lower-heating-value (LHV) basis, with 95% CO_2 capture. The projected 400-MW coal-fired power plant would have a LHV new efficiency of 44%, with 98% CO_2 captured (Bryngelsson and Westermark, 2005).

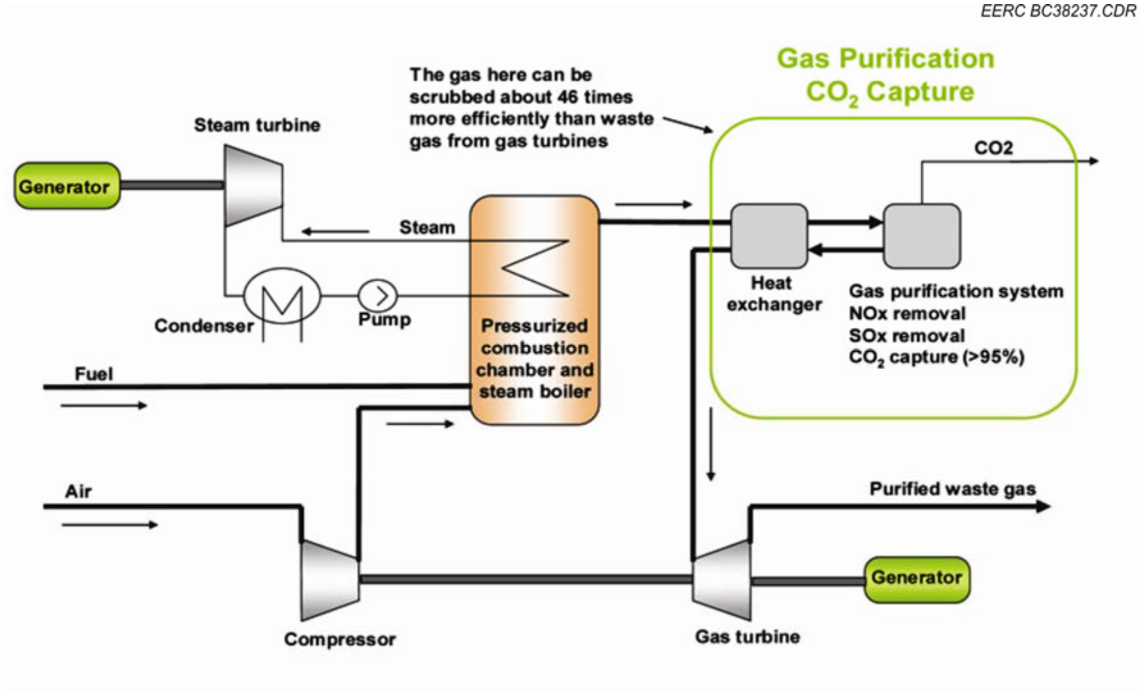

Figure 22. Sargas process (taken from Sargas AS, 2010).

The technology was demonstrated at pilot scale in 2007 and early 2008 at a coal-fired power plant in Stockholm (Bryngelsson and Westermark, 2009), and a 1-MW pilot-scale power plant demonstration is currently in preparation in South Park, Pennsylvania. The South Park project is a partnership between Sargas AS; Environmental Energy Technology, Inc. (EET); and CONSOL Energy, Inc. A PFBC–EET clean coal technology system will be used to generate power from waste coal and other fuels. This pilot project is located at CONSOL Energy's R&D facilities and received a $1.64 million grant from the Pennsylvania Department of Environmental Protection (DEP) (CONSOL Energy, 2010).

Sargas AG has also made an alliance with Daewoo Shipbuilding & Marine Engineering Co. Ltd. (DSME) of Korea to build and install their first 100-MW natural gas plant in Hammerfest, Norway. They hope also to build their first 400-MW coal plant in west Norway in the near future (Daewoo Shipbuilding & Marine Engineering Co. Ltd., 2009). Additional information on the Sargas process can be found on the Sargas Web site (Sargas AS, 2010) and in Bryngelsson and Westermark (2005), McRae and de Meyer (2006), and Siemens Power Generation (2006).

Siemens POSTCAP™ Process

Siemens has developed a postcombustion CO_2 capture process called the POSTCAP process that is based on the use of an amino acid–salt solution as the chemical absorbent (Jockenhoevel and others, 2009). This technology was developed by Siemens and the power company E.ON through the German Federal Ministry of Economics and Technology-funded POSTCAP project. The solvent features include a high CO_2 capture rate, low-energy demand, a low rate of solvent degradation, production of a high-purity CO_2 stream, and low environmental risk (Jockenhoevel and others, 2009).

The salts of amino acids react with CO_2 in much the same way as normal amines, i.e., by carbamate, carbonate, and bicarbonate formation (as shown in Figure 23) and have low sensitivity to degradation by oxygen and temperature (Jockenhoevel and others, 2009).

The amino acid–salt solution is used in a conventional absorber–stripper capture process that Siemens has modified with respect to material integration, energy integration of the compression unit, and integration with the power plant in order to exploit the potential for minimizing the carbon capture cost. Siemens reports that its amino acid–salt-based solvent used in a conventional process would consume 0.97 MWh/ton CO_2. This is estimated to decrease to 0.64 MWh/ton of CO_2 using the improved process (Jockenhoevel and others, 2009) The currently estimated CO_2 capture costs (including CO_2 compression but without transport and storage) are approximately \$44/ton of CO_2 in the early commercial phase (i.e., prior to 2020) and approximately \$30/ton of CO_2 in the mature commercial phase (before 2030) (Jockenhoevel and others, 2009).

Siemens and E.ON started a pilot CO_2 capture facility in late September 2009 at an E.ON power plant near Frankfurt, Germany. The test will run until the end of 2010. The results achieved and the operating performance of the pilot plant will serve as the basis for the large-scale Fortum Meri-Pori Demonstration Plant (Finland) scheduled to begin operation in 2015. CO_2 capture is planned to be performed on 50% of the flue gas for this 565-MW facility. In June

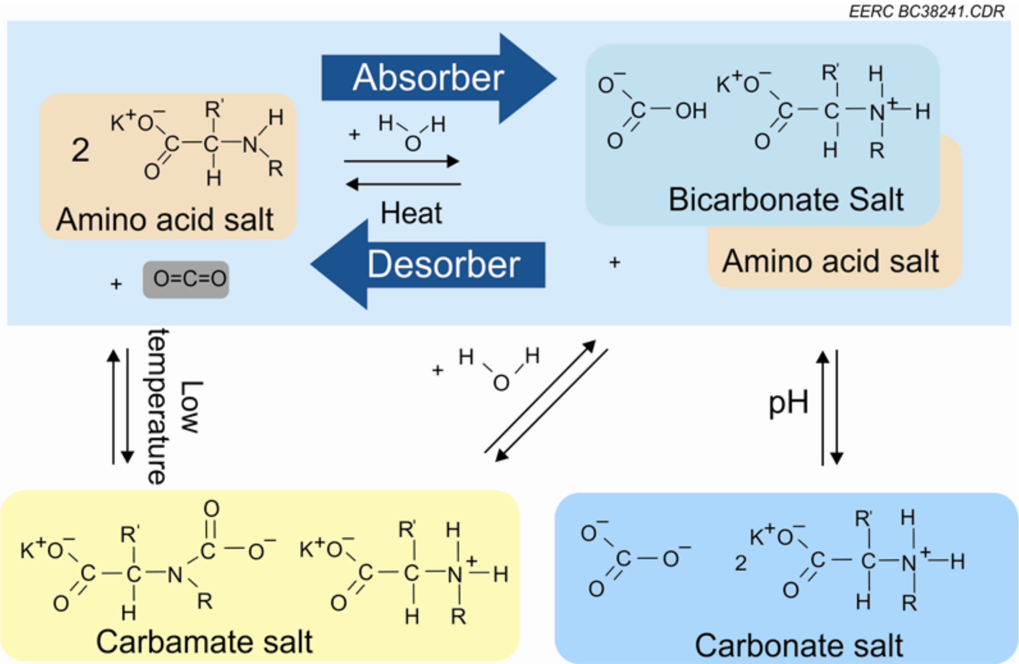

Figure 23. Amino acid–salt absorption reaction scheme (taken from Jockenhoevel and others, 2009).

2009, Siemens signed an agreement with TNO, the Netherlands Organization for Applied Scientific Research, aimed at the further advancement of the second generation of the amino acid–salt-based carbon capture technology (Siemens Energy and TNO, 2009). TNO has a long history of work on the development and use of amino acid salts for CO_2 capture applications.

On July 7, 2010, DOE announced that it will provide funding for Siemens Energy to design, install, and operate a pilot plant for treating a slipstream (1 MW equivalent) at the TECO Energy Big Bend Station (Tampa, Florida) to demonstrate POSTCAP technology for postcombustion CO_2 gas capture (U.S. Department of Energy, 2010a).

Developing Technologies for Chemical Absorption

Use of Mass Transfer Devices Other than Absorption Towers

For the chemical absorption solutions having very fast reaction kinetics, there can be substantial benefits derived from increasing the amount of gas–liquid contact area present in a given volume of the absorption and/or stripping vessel. This can be done in a variety of ways, two of which are presented here: the use of membrane contactors and the use of a liquid jet contactor.

Membrane Contactors

Membrane contactors are flat-sheet, spiral-wound, or hollow-fiber membrane modules in which a porous membrane is used to separate the gas phase from an absorption solution. These can offer very high surface areas (1000 m^2/m^3 or more) for mass transfer in a small volume and can permit the use of solvent solutions that might not work well in an absorption tower because of the tendency to foam or froth. A tenfold decrease in absorber volume is possible. Figure 24 is an illustration of a hollow-fiber membrane absorber where the gas flow path is on the shell side of the hollow-fiber tubes. The absorbing gas passes through the pores in the membrane and dissolves in the absorption solvent, which is pumped through the bores of the hollow fibers. Several entities have investigated the use of membrane contactors. Only a few examples are given here.

Kvaerner Hybrid Membrane Absorption System (KHMAS)

The KHMAS is a gas–liquid membrane contactor that replaces a traditional absorber. The KHMAS was developed by Kvaerner Process Systems, which has since merged with Aker Process Systems. In the KHMAS, CO_2 diffuses through a microporous, hydrophobic polymer membrane into a flowing liquid. The solvent, rather than the membrane, provides the selectivity. The KHMAS weighs 70% less and has a 65% smaller footprint than a conventional absorber. The membranes used are flat-sheet polytetrafluoroethylene (PTFE) membranes from W.L. Gore & Associates, Inc. A large number of membrane types were tested during development, but the amines destroyed some and wetted others, causing blockage of the membrane pores and/or leakage of solvent into the gas flow path (Falk Pedersen and Imai, 2003).

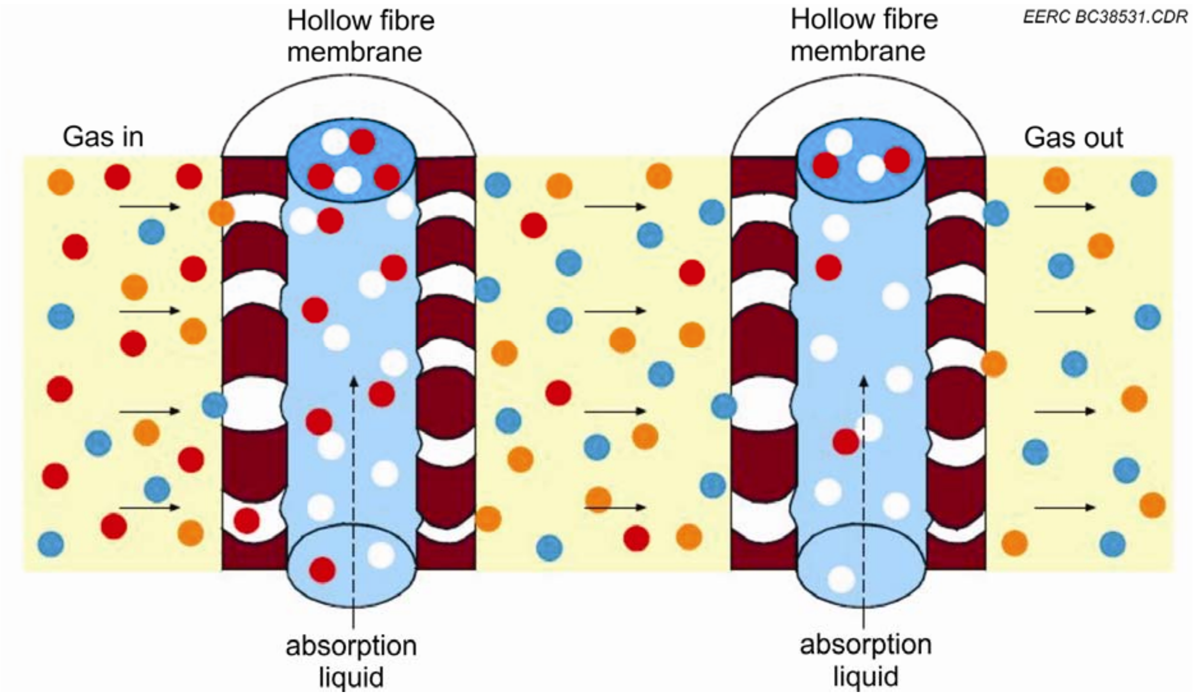

Figure 24. Membrane absorption with gas on shell side (taken from ten Asbroek and Feron, 2004).

The system was developed, modeled, scaled up, and pilot-tested between 1993 and 2004. Testing of the KHMAS included work on natural gas sweetening, dehydration, and CO_2 removal from flue gas. A flue gas pilot project using MHI's KS-1 solvent and the KHMAS at MHI's Nankotest facility in Japan found a statistically insignificant capital cost savings and a 19% operating cost savings for CO_2 capture versus MEA used in a conventional system (CO_2 Capture Project, 2004).

PoroGen Carbo-Lock™ Process for CO_2 Capture

The PoroGen Carbo-Lock process is based on the use of a new fluorocarbon surface-modified polyether ether ketone (PEEK) hollow-fiber membrane contactor (Zhou and others, 2010). The porous membrane was developed to be extremely hydrophobic in order to avoid the pore wetting that has been observed for other hydrophobic membranes such as polyolefins like polypropylene and, to a lesser extent, PTFE. The membrane contactor was introduced by the PoroGen Corporation in 2008–2009. PoroGen is currently working with the Gas Technology Institute (GTI) to test the membrane absorber on various physical and chemical solvents at both high and low gas feed pressures.

On July 7, 2010, National Energy Technology Laboratory (NETL) announced that it was funding a 3-year development project with GTI, PoroGen, and Aker Process Systems to develop cost-effective hybrid separation technology for CO_2 capture from flue gases based on a combination of absorption and hollow-fiber membrane technologies (U.S. Department of Energy

National Energy Technology Laboratory, 2010h). Therefore, it appears that the project will investigate the use of the PoroGen membrane in place of the PTFE membrane material in the KHMAS.

TNO Membrane Absorber and CATO CO_2 Catcher

TNO is a company headquartered in the Netherlands that has been involved in carbon capture technology development for postcombustion capture through its work using amino acid salt-based solvents that they refer to as CORAL solvents (Goetheer, 2009; Feron and ten Asbroek, 2004). TNO applies these solvents in tower-based absorber–strippers and in systems that incorporate the use of membrane absorbers. The TNO membrane absorber is 5 to 10 times smaller than equivalent packed columns, which would reduce capital cost (Peters, 2009). The membranes used in the TNO absorbers are made of polyolefins (e.g., polypropylene). As noted earlier, TNO and Siemens are cooperating on further development of processes for CO_2 capture based on the use of amino acid salts (Siemens Energy and TNO, 2009).

Since April 2008, TNO has operated the CATO CO_2 Catcher, a CO_2-from-flue gas capture pilot plant, at E.ON Benelux's power plant near Rotterdam. (CATO is the Dutch national R&D program for CO_2 capture, transport, and storage.) The pilot test results indicate that the solvent is remarkably stable under industry conditions, has a high capture rate, and compares favorably in terms of energy consumption to the MEA standard. Cost of CO_2 avoided and energy penalty relative to the MEA benchmark are indicated in Figure 25 (Goetheer, 2009).

Additional information on the CATO CO_2 Catcher project and the TNO membrane absorber is available at multiple sources (Allaie and Jaspers, 2008; TNO, 2010; Feron and Jansen, 2002; Goetheer, 2009).

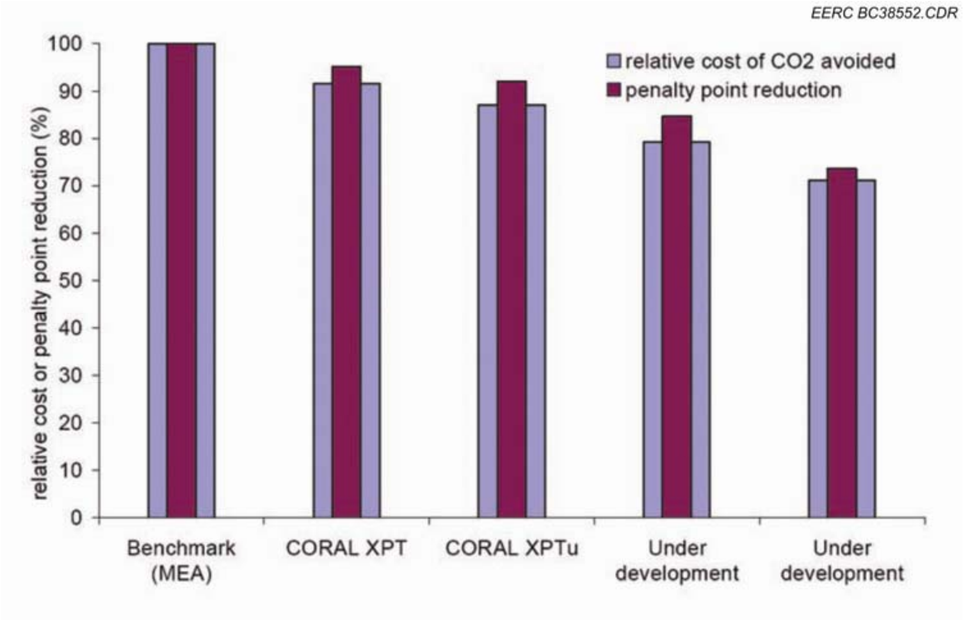

Figure 25. Cost comparison of CORAL solvents to MEA (taken from Goetheer, 2009).

University of Kentucky Research Foundation's Solvent–Membrane Hybrid Postcombustion CO_2 Capture Process

A research team at the University of Kentucky was recently awarded a DOE Advanced Research Projects Agency – Energy (ARPA-E) project to develop a hybrid absorption solvent–catalytic membrane for use in a postcombustion CO_2 capture process (U.S. Department of Energy Advanced Research Projects Agency – Energy, 2010a). The project description states that the membrane will be a catalytic separator that couples nanofiltration separation and catalysis. It is not clear if this will be a membrane contactor with catalytic activity or a liquid membrane permeator with catalytic activity.

Neumann Systems Group, Inc., Liquid Jet Contactor – NeuStream^{TM}–C

The Neumann Systems Group, Inc. (NSG), is a technology and development company that is focused on gas–liquid contact systems for chemical processing and emission control. NSG has developed an integrated environmental control technology called NeuStream^{TM}–S that has shown promise as a low-cost option for SO_2 control for coal-fired boilers. The process consists of a unique horizontal flow absorber that produces very high mass transfer rates while reducing the overall footprint and energy consumption. A unique nozzle design produces flat jets of absorber liquid (in the case of SO_2 control, NSG uses a sodium hydroxide solution) that substantially increase the surface area available for mass transfer by a factor of 10 over conventional spray systems. The gas is injected in between the jets and parallel to the faces of the jets. This configuration permits higher gas throughput without disrupting the jets or entraining liquid droplets into the gas. The enhanced mass transfer and increased throughput of gas result in smaller contactor/duct volumes and reduced manufacturing costs (Neumann and others, 2010). NSG is extending the process to the future capture and processing of CO_2 in a device called NeuStream–C.

NSG claims that the improved mass transfer that is achieved in its treatment technology will result in a substantially smaller treatment unit (by as much as a factor of 15), resulting in significantly reduced capital investment. Because it is anticipated that less absorber liquid will be required to achieve the desired removal, the operating costs for the gas treatment are also expected to be substantially less.

The mass transfer system should provide the stated benefits when working with a high-concentration, high-pH solution with fast reaction kinetics (such as a hydroxide solution). The difficulty with respect to the use of the system for CO_2 capture versus SO_x removal is the need to regenerate the solvent. Orders of magnitude more CO_2 than SO_x must to be removed from coal-fired power plant flue gas, and the rate of CO_2 mass transfer is lower because of its lower reaction rate. Suitable absorber liquids must be identified for the NeuStream–C to be applied to CO_2 capture. This type of testing using the NeuStream-C will be performed by the EERC's Partnership for CO_2 Capture (PCO_2C). Further information on the NeuStream process can be found in multiple sources (Colorado Springs Utilities, 2009; Colorado Springs Gazette, 2008a–c, 2009; Electric Power Research Institute, 2008, 2010; Neumann Systems Group, Inc., 2009).

Use of Other Solvents in Absorber–Stripper Systems

Use of Piperazine

Dr. Gary Rochelle's group at the University of Texas has done a considerable amount of work on the use of piperazine (PZ), an organic compound that contains two secondary amine groups, as a chemical absorbent alone in high concentration (Rochelle and others, 2010; Freeman and others, 2010a, b) and in combination with potassium carbonate (U.S. Department of Energy National Energy Technology Laboratory, 2010a; Cullinane and Rochelle, 2004). PZ has also been added to MEA and MDEA, where it acts primarily as a promoter, increasing CO_2 absorption rate (Dang and Rochelle, 2001; Cullinane and Rochelle, 2004).

The PZ-promoted potassium carbonate process has been studied at small pilot scale by the Rochelle group and by Kather and Oexmann (2008). It promises lower-cost treatment compared to MEA because of a lower heat duty for solvent regeneration and the use of much lower temperatures for solvent regeneration (131°F compared to 248°F for MEA), which allows for the use of waste heat rather than steam taken from the low-pressure (LP) turbine inlet. Some concerns remain about the need for foaming control and the fact that the amount of CO_2 transported per unit volume of solution per cycle is lower than that of a 30 wt% MEA solution. This would require a larger column diameter, although this would be offset by the shorter column heights afforded by the fast PZ kinetics. Economic analysis of the system indicates a lower investment cost.

More recently, the Rochelle group has been promoting the use of concentrated PZ (40 wt%). The use of this solution would permit absorption towers to be shorter and smaller in diameter because the absorption capacity is 1.8 times that of 30 wt% MEA and the mass transfer rate is double that of 30wt% MEA. In addition, PZ is thermally stable when regenerated by distillation, is resistant to oxidation, and has a lower volatility, making it easier to prevent its loss to the atmosphere. The energy cost of concentrated PZ is 10% to 20% lower than that for MEA, and the CO_2 product is generated at 11 to 17 atm (at 150°C), thus reducing compression costs (Rochelle and others, 2010).

A recently announced DOE-funded project by the URS Group and partners will investigate the use of concentrated PZ at a scale of 0.1 MW equivalent and then at a scale of 0.5 MW (U.S. Department of Energy National Energy Technology Laboratory, 2010h). The larger-scale test will be conducted at DOE's National Carbon Capture Center. It is likely that this project will involve Gary Rochelle's group because URS is one of the funding partners of his Luminant Carbon Management Program (Rochelle, 2009).

Enzyme-Based Catalysts

The carbonic anhydrases are metalloenzymes (most commonly containing zinc) that catalyze the conversion of CO_2 to bicarbonate ions, HCO_3^-, and hydrogen ions, H^+. There are several classes of carbonic anhydrases with significantly varied protein form, but all with a common function: to catalyze the conversion of CO_2 to bicarbonate. This conversion is carried out by the enzyme first reacting with water to split it into a hydrogen ion and an enzyme-associated zinc hydroxide and the subsequent reaction of the zinc hydroxide form of the enzyme with CO_2 to form the bicarbonate ion. Because the rate of reaction of hydroxide ions with CO_2 is very fast compared to the rate of the combined hydration of CO_2 to carbonic acid, $CO_2 + H_2O \rightarrow H_2CO_3$, and subsequent dissociation of carbonic acid to hydrogen ions and bicarbonate, the enzyme is able to speed the reaction significantly in solutions with low hydroxide ion availability (typically, a benefit at pH <10). The enzyme also catalyzes the reverse reaction of combining hydrogen ions and bicarbonate to yield CO_2 and water. In order to be of most benefit, the catalyst needs to be present at the gas–liquid interface. This presents a challenge with respect to engineering a system based on use of the catalyst while providing for long life of the enzyme.

Several companies are developing technologies based on the use of carbonic anhydrase for CO_2 capture. These efforts include improvements in the enzyme form and function, development of methods for use of the enzyme in an engineered system, and development of specialized mass transfer devices to take advantage of the enzyme function; one group is even developing a synthetic analog of the enzyme's active site and ways to use this catalyst.

Akermin – Immobilization of Carbonic Anhydrase

Akermin, Inc., is a large enzyme development and supply company that is developing a carbonic anhydrase immobilization–stabilization method for use in CO_2 capture from flue gas (Akermin, Inc., 2009). The concept is to encapsulate the enzyme within tailored polymer structures, which protects the enzyme, allowing for long lifetime. In addition, the enzyme is distributed in the capture solution so that it is present at the gas–liquid interface, where it will provide the most benefit. Figure 26 is a conceptual drawing of the enzyme contained in the polymer structure. Akermin has been working on the technology for approximately 5 years and was recently awarded a 2-year project to optimize its enzyme-containing solvent formulation and demonstrate process efficacy by treating up to 2000 standard liters of simulated flue gas per hour. (U.S. Department of Energy National Energy Technology Laboratory, 2010h).

Carbozyme – Contained Liquid Membrane Permeator and Membrane Absorber–Stripper

Carbozyme, Inc., is a small technology development company that has been developing carbonic anhydrase-based CO_2 removal systems for advanced life support applications as well as systems for CO_2 capture from air and flue gas. Carbozyme's systems are based on the use of hollow-fiber membrane-based modules (Trachtenberg and others, 2005). The treated gas and product gas flow through the bores of two sets of hollow fibers, one for the flue gas and one for the product gas. The hollow fibers are separated by a liquid that acts as the permeance-selective membrane. The enzyme carbonic anhydrase is immobilized to the shell side of the hollow-fiber membranes in order to be present at the gas–liquid interface. The enzyme enables faster transport of the CO_2 by catalyzing the conversion of CO_2 to bicarbonate at the flue gas–liquid interface and bicarbonate to CO_2 at the liquid–product gas interface. A vacuum-assisted water vapor sweep provides the low CO_2 partial pressure on the product side necessary to maintain a favorable driving force for CO_2 transport through the liquid membrane. A schematic of this system, called a contained liquid membrane permeator, is shown in Figure 27.

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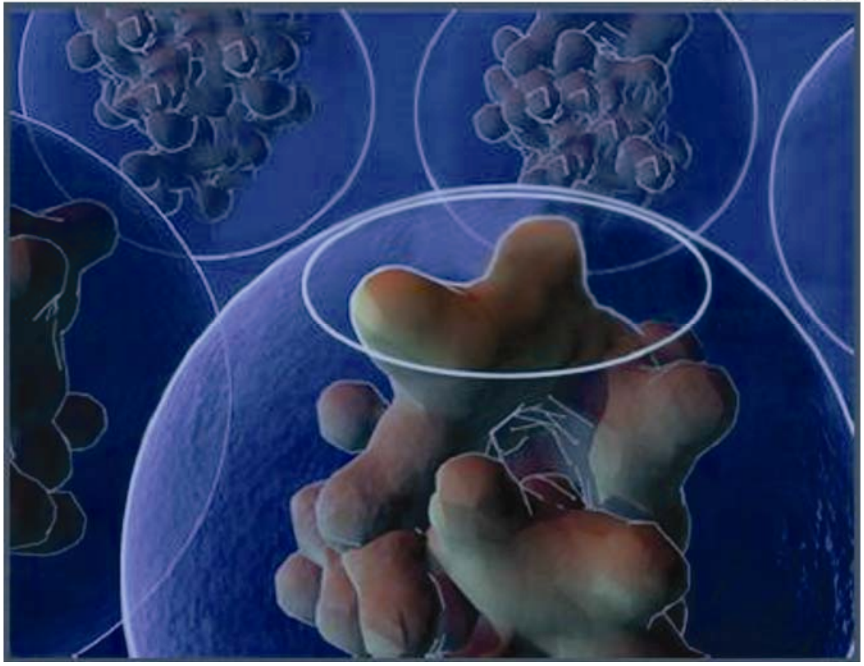

Figure 26. Akermin immobilized carbonic anhydrase (taken from Akermin, Inc., 2009).

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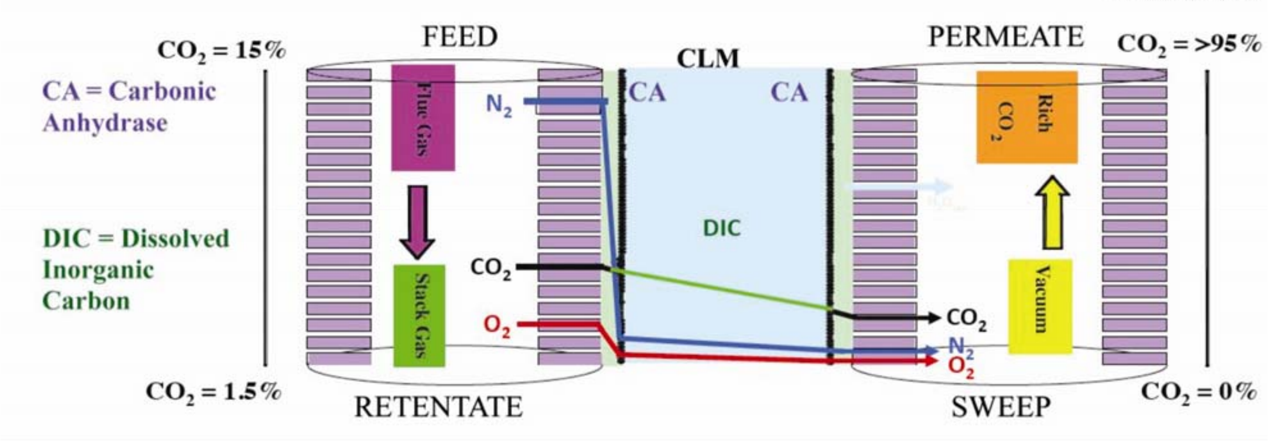


Figure 27. Conceptual illustration of the Carbozyme contained liquid membrane permeator (taken from Smith and others, 2010).

Most recently, Carbozyme has reported on the use of a proprietary absorber–stripper arrangement based on the same concept of using carbonic anhydrase immobilized at the gas–liquid interface (Smith and others, 2010). This configuration is shown in Figure 28.

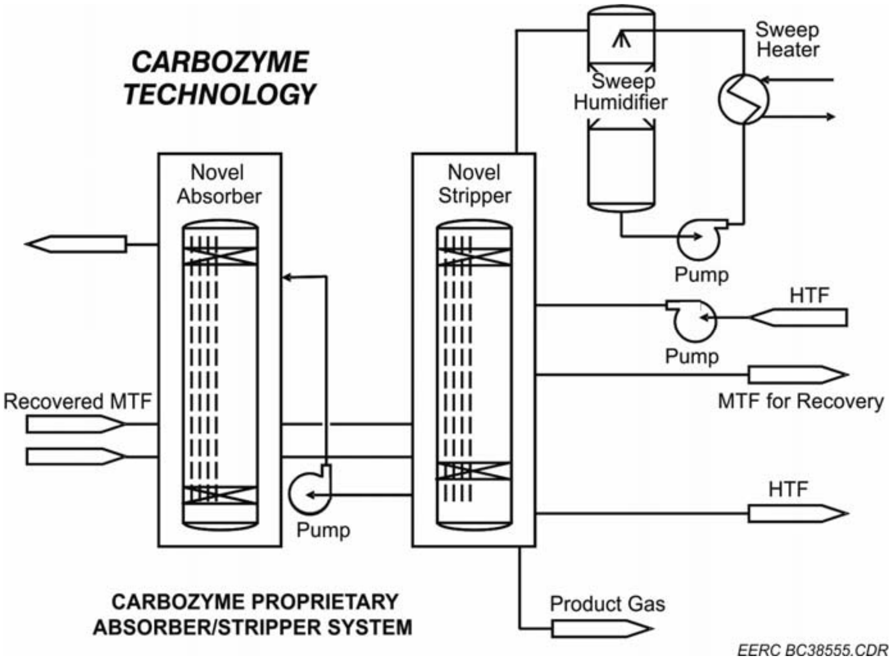


Figure 28. Carbozyme proprietary absorber–stripper system (after Smith and others, 2010; Carbozyme, Inc., 2010).

CO_2 Solution – Enzyme-Enhanced Amines

CO_2 Solution, Inc., has been developing CO_2 capture systems based on the use of the enzyme carbonic anhydrase in packed-bed absorption tower-type absorber–stripper systems (CO_2 Solution, 2009). This concept allows solutions with low regeneration temperatures but also having low rates of absorption to be viable candidates for postcombustion capture. Initially, the company worked to immobilize the enzyme to the tower packing and studied the benefit of the presence of the enzyme on the rate of CO_2 absorption into metal carbonate and amine solutions. The location of the enzyme at the liquid–solid interface rather than the gas–liquid interface limited the benefit derived from the enzyme. Recently, CO_2 Solution moved to immobilization of the enzyme onto nano-sized carriers that allow the enzyme to be transported in the absorption solution and, therefore, to be present at the gas–liquid interface (CO_2 Solution, 2009). Figure 29 illustrates the relative improvement in absorption rate derived from the use of this free-flowing enzyme compared to the use of the enzyme immobilized to the packing and the no-enzyme condition for solutions of 4 M MDEA and 1.45 M potassium carbonate. Figure 30 compares the free-flowing immobilized enzyme with the no enzyme condition for MEA, MDEA with a chemical promoter, an amino acid salt, MDEA, and a carbonate solution. The greatest benefit is derived for the solution with the slowest noncatalyzed absorption rate. CO_2 Solution is still doing laboratory-scale testing. Larger-scale integrated-system bench testing is planned for the period 2010 to 2012. Small-scale pilot testing and demonstration is planned for 2012 to 2014.

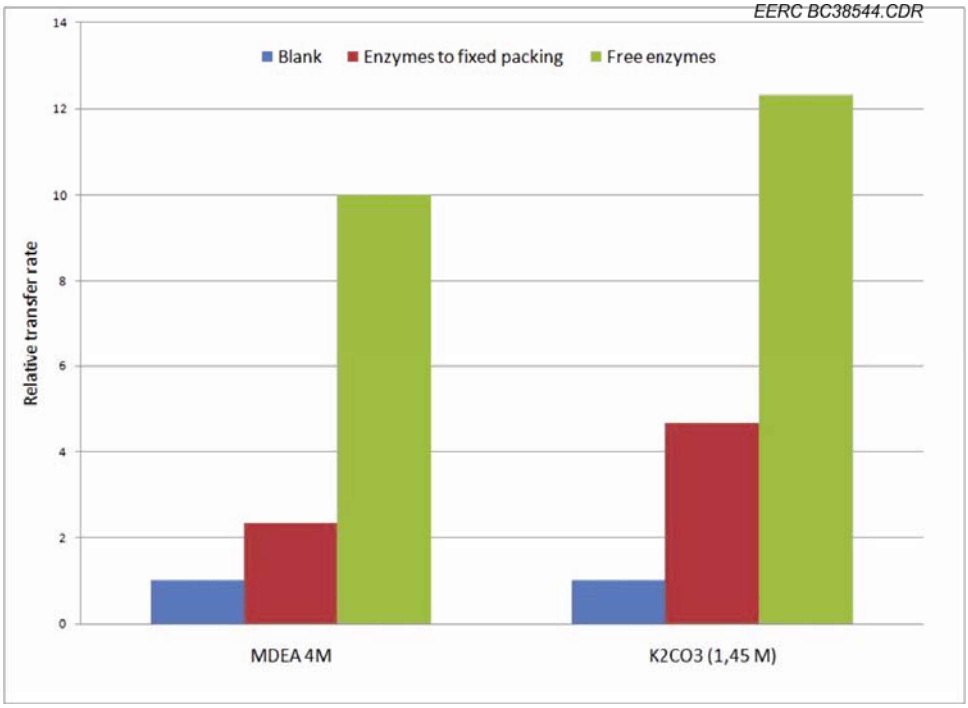


Figure 29. Relative CO_2 transfer rate using no enzyme (blue), enzyme immobilized to column packing (red), and enzyme suspended in solution (green) (taken from CO_2 Solution, 2009).

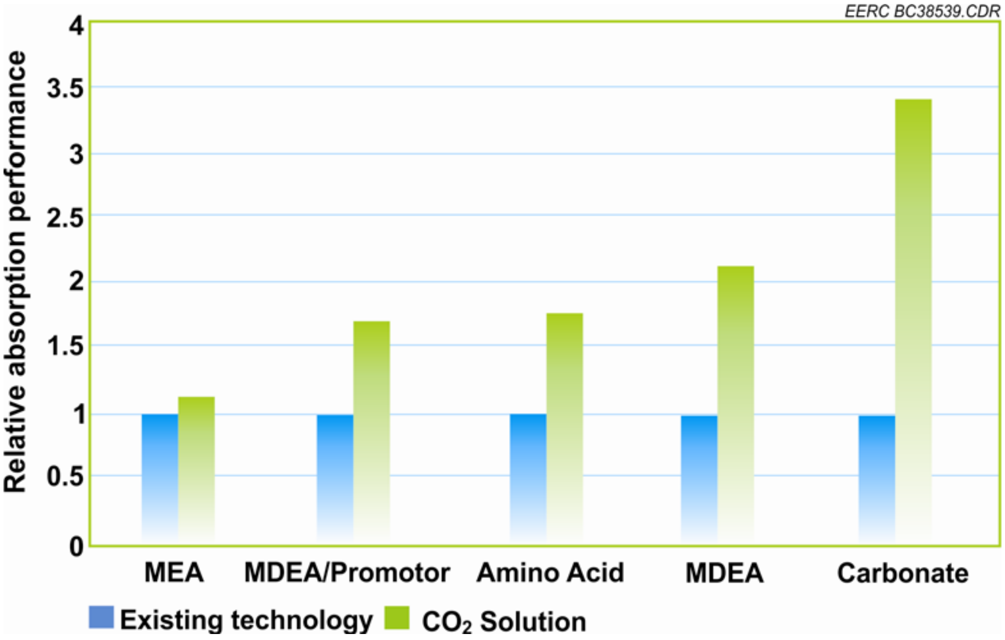


Figure 30. Relative improvement in CO_2 absorption observed in five chemical absorption solutions (taken from CO_2 Solution, 2009).

CO_2 Solution has entered into a joint development agreement with Codexis, a major enzyme supplier and developer. They will work together on a Codexis-led project recently funded under a DOE ARPA-E Innovative Materials & Processes for Advanced Carbon Capture Technologies (IMPACCT) project entitled Low-Cost Biological Catalyst to Enable Efficient CO_2 Capture (U.S. Department of Energy Advanced Research Projects Agency – Energy, 2010e; Codexis, Inc., 2010).

Integrated Vacuum Carbonate Absorption Process

The research and development team at the Illinois State Geological Survey (ISGS) is using carbonic anhydrase as a catalyst to increase the rate of absorption and stripping of CO_2 in its integrated vacuum carbonate absorption process (IVCAP) for postcombustion CO_2 capture. The process is an absorption tower–stripper system that uses a potassium carbonate solution as the chemical absorbent. Carbonic anhydrase is used as a catalyst (promoter), and the steam requirement for stripping and stripping temperature are decreased by desorbing the CO_2 under low-pressure (vacuum) conditions. Stripping at low temperature allows the use of low-quality steam (close to the exhaust end of the low-pressure turbine). Integration of the patented process into a pc power plant is shown in Figure 31.

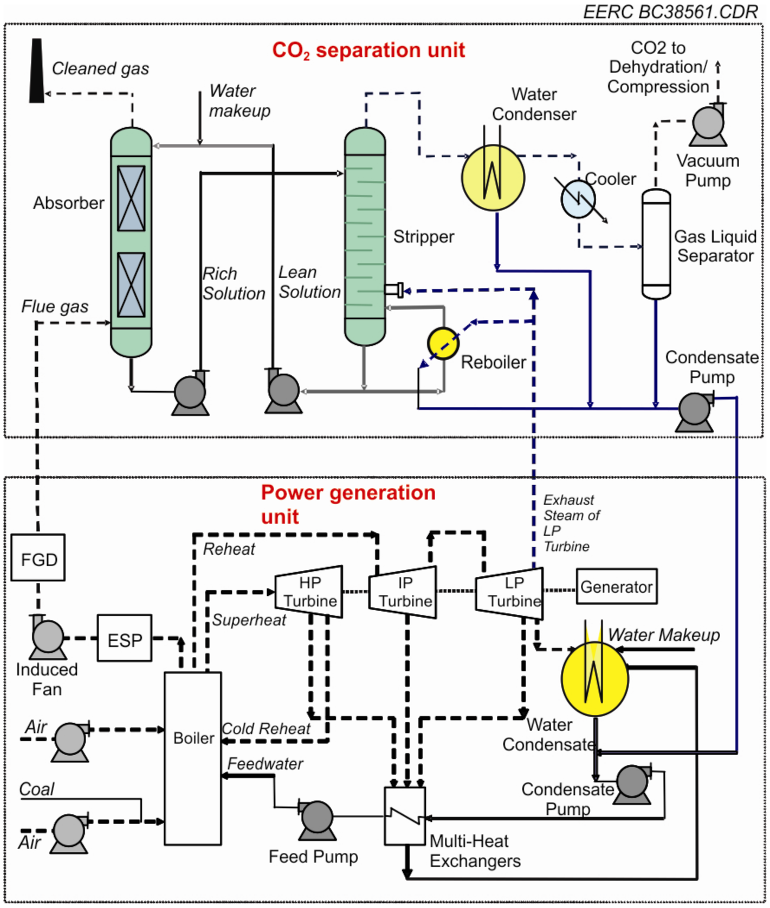


Figure 31. IVCAP process (taken from Chen and others, 2006).

Process simulations indicated that the process would reduce the electricity generation of a 533-MW-gross-output coal-fired power plant by 35.6 MW, compared to a 96.3-MW reduction with the use of 30% MEA. The calculated CO_2 avoidance costs from the process simulations were $30.9/ton CO_2 using IVCAP and $41/ton using MEA (Chen and others, 2006; Chen and Lu, 2007; Lu, 2009; U.S. Department of Energy National Energy Technology Laboratory, 2009a). The research team recently reported progress on the immobilization of carbonic anhydrase for use in the process (Lu and Rostam-Abadi, 2010).

Novozymes – Heat-Stable Carbonic Anhydrase

Novozymes is a major enzyme development and manufacturing company that holds a patent (W02010014774A2) for the use of a membrane-based system for CO_2 capture using solutions containing carbonic anhydrase and has submitted a patent application (US2010047866A1) related to high-temperature carbonic anhydrase for use in CO_2 capture from flue gas.

Synthetic Catalysts Based on Carbonic Anhydrase Active Site

A research group at Lawrence Livermore National Laboratory has been working to develop small synthetic chemical molecules that mimic the catalytically active site of carbonic anhydrase for use in CO_2 capture applications. Recently, this group teamed with researchers at the University of Illinois and Babcock & Wilcox to propose an ARPA-E-funded project that will be led by the United Technologies Research Center. The project is entitled "Catalytic Improvement of Solvent Capture Systems" and will focus on furthering the development of these small-molecule catalysts and demonstrating their effective use under a range of process conditions (U.S. Department of Energy Advanced Research Projects Agency – Energy, 2010c).

The compounds being studied are synthetic organometallic chemicals. Figure 32 (Lawrence Livermore National Laboratory, 2010) is an illustration of the enzyme carbonic anhydrase, the catalytic center, and the small-molecule catalysts, which mimic the zinc complex that serves as the catalytic center. Davy (2009) provides additional information on these types of compounds.

New Absorbents for CO_2 Capture

Ionic Liquids or Room-Temperature Ionic Liquids (RTIL)

Ionic liquids, or more accurately room-temperature ionic liquids (RTIL), are organic salts that are liquid at or near room temperature. Some ionic liquids are physical absorbent CO_2 solvents. Ionic liquids containing amine functional groups are chemical CO_2 solvents. The physical absorbent type of ionic liquids have relatively low heats of absorption, and similar to other physical absorbents, the loading capacity is very low under postcombustion flue gas conditions. This means that physical absorbent ionic liquids by themselves are not good candidates for postcombustion CO_2 capture but, instead, may be good candidates for use in precombustion capture. When mixed with amines, physical solvent ionic liquids can be used for

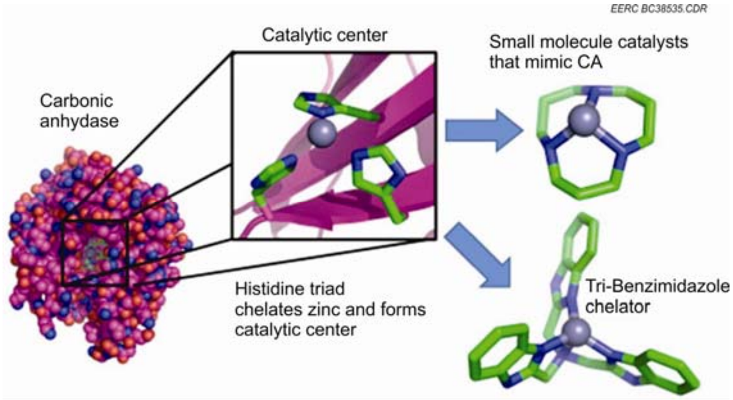


Figure 32. Synthetic small-molecule catalysts based on the active center of carbonic anhydrase (taken from Lawrence Livermore National Laboratory, 2010).

postcombustion capture. In this case, the ionic liquid acts as the bulk solvent in place of water and the amine acts as the chemical solvent.

Chemical absorbent ionic liquids containing amine functional groups are good candidates for postcombustion CO_2 capture. Because RTILs are liquid salts of organic compounds, there is an almost infinite variety of potential molecular structures, meaning that RTILs can be engineered to have different properties for different applications and thus can be considered "designer solvents." Many university and corporate research groups are involved in designing, synthesizing, and testing new RTILs for use as absorbents in CO_2 capture applications. In addition to the use of the ILs as liquid absorbents, there are efforts in the use of the ILs in liquid membranes, as gels in membranes, and as the basis for polymers that are used to build solid sorbents and membranes that can be used for gas separations.

Additional information on the physical and chemical absorption of CO_2 into ionic liquids is available in papers published by researchers from DuPont (Yokozeki and others, 2008) and Eindhoven University in the Netherlands (Galán Sánchez, 2008). A brief overview of the efforts of some of the entities working in this area is given in the following text.

ION Engineering, LLC

ION Engineering, LLC, is a company founded by members of a research group at the University of Colorado that has been working on CO_2 capture using ionic liquids. The group has licensed technology from the University of Colorado for the use of IL–amine mixtures. The company is working to integrate ILs into solvent-based gas processing, including flue gas carbon capture and natural gas treatment. ION Engineering recently landed a 15-month ARPA–E-funded project to use a physical solvent ionic liquid–amine mixture in a bench-scale carbon capture unit (U.S. Department of Energy, 2010a). The unit will be operated on a slipstream of flue gas at an operating power plant.

University of Notre Dame

The DOE-funded research group at the University of Notre Dame has published many papers and reports on its work in the development of RTILs for postcombustion CO_2 capture. In the most recent paper, Gurkan and others (2010) report success with the design and synthesis of ILs that react with CO_2 in a 1:1 stoichiometry, meaning that higher molar capacities have been achieved. The paper also shows that changing the location of functional groups on these types of ILs can change the reactivity, indicating that functionalized ILs can be designed for specific applications.

Additional work by the research group at the University of Notre Dame includes collaboration with Air Products and Chemicals, Babcock & Wilcox, DTE Energy, Merck/EMD Chemicals, and Trimetric. Recently, Trimeric completed a systems analysis for CO_2 capture based on IL properties derived from the University of Notre Dame work (Myers and others, 2010). Trimeric determined that the CO_2 capture from a pc-fired plant using ILs would have a cost of electricity of 8.8¢ to 9.5 ¢/kWh where the base cost of electricity was 5 ¢/kWh without CO_2 capture and 10.6 ¢/kWh with MEA- based CO_2 capture. In other words, CO_2 capture using ILs having the properties specified in the study was estimated to be 11% to 17% lower than that for capture using MEA.

While working on the liquid solvent ILs, Notre Dame researchers discovered a class of ionic liquid compounds that are solids until their reaction with CO_2 causes a phase change to a liquid state. This behavior presents interesting possibilities for the development of novel CO_2 capture processes. The group has received funding through ARPA–E IMPACCT to synthesize and study more examples of this new class of compounds (U.S. Department of Energy Advanced Research Projects Agency – Energy, 2010b). Additional sources of information for the University of Notre Dame work on ILs include Maginn (2005a,b, 2008, 2009).

University of Colorado

The research group at the University of Colorado that is working on CO_2 capture developed the IL plus amines solution technology, which has been licensed to ION Engineering. Additional information on the technology and other aspects of the work are available in the 2009 review paper on imidazolium-based RTILs (Bara and others, 2009). Most of the other work the group has done on ionic liquids involves the use of ILs in supported liquid membranes, composite membranes, and in the development of imidazolium-based polymers (Bara and others, 2010; Carlisle and others, 2010). The ionic liquid-based membrane work is covered in the section on membrane separations.

University of Wyoming

Researchers at the University of Wyoming are working with a class of IL-based compounds that they refer to as poly(ionic liquid)s. These are solid polymers made by polymerizing imidazolium-based IL monomers. The researchers report that the poly(ionic liquid)s have higher CO_2 sorption capacities than RTILs, faster sorption–desorption rates, and can be applied in novel sorbent and membrane material applications. The poly(ionic liquid)s rapidly dissolve gaseous CO_2 and release it when the pressure is reduced to vacuum levels. It was found that the CO_2 sorption capacity of poly(ionic liquid)s primarily depends on the chemical structure, while the rate of CO_2 sorption is affected by the surface area of the polymers.

A series of ionic liquid monomers and their polymers having different cation and anion structures were synthesized and characterized. The CO_2 absorption capacities ranged from 2.7 to 10.2 mol% (Tang and others, 2005a). Poly(ionic liquid)s with higher polar cations and anions have higher CO_2 solubility. Crosslinking of the polymer decreased the CO_2 absorption capacity of poly(ionic liquid)s.

Advantages of poly(ionic liquid)s include absorption capacities that are 6.0 to 7.6 times those of RTILs; quick, complete desorption under vacuum; selective sorption of CO_2 (i.e., O_2 and N_2 are not absorbed on the material), and limited adverse effects from moisture (Tang and others, 2005c). The technology is currently expensive because of the expense of vacuum desorption on a large scale and because poly(ionic liquid)s are not manufactured commercially.

More information on the poly(ionic liquid) work by researchers at the University of Wyoming can be found in papers by Tang and others (2005b, 2009).

Georgia Institute of Technology

Researchers at Georgia Institute of Technology (Georgia Tech) have been studying two different IL-based CO_2 capture technologies: one-component reversible ionic liquid solvent for CO_2 capture and high-performance CO_2 scrubbing based on hollow-fiber-supported designer ionic liquid sponges. The first is a liquid sorbent technology, while the second is a hybrid solid sorbent-type technology (mixed absorption/adsorption).

Reversible IL solvents are liquids that change from molecular liquids to ionic liquids because of mild changes that are applied to the solution. An example is shown in Figure 33 where CO_2 acts as the agent of change. The compound shown in Figure 33 was exposed to gaseous CO_2 at 1 atm and exothermically converted from the molecular liquid phase to an ionic liquid. Stripping off the CO_2 using inert gas or heating it to 50°–60°C converts it back to a neutral liquid (Fadhel and others, 2009). The current work on the project is funded by DOE (U.S. Department of Energy National Energy Technology Laboratory, 2009e). Updates on the progress of the project are available on the Georgia Tech project Web site (Georgia Institute of Technology, 2010).

The concept of high-performance CO_2 scrubbing based on hollow-fiber-supported designer ionic liquid sponges involves trapping ionic liquids inside hollow polymer fibers. The hollow fibers would be used in either a temperature- or pressure swing adsorption-type system. This project was funded under ARPA–E and is centered at Oak Ridge National Laboratory (ORNL) (U.S. Department of Energy Advanced Research Projects Agency – Energy, 2010f).

GE Global Research

Two DOE-funded research projects on improved solvents for CO_2 capture are being performed by GE Global Research. The first of these, funded through the existing plants program, is an investigation centered on synthesis of new liquid absorbents entitled "Novel High

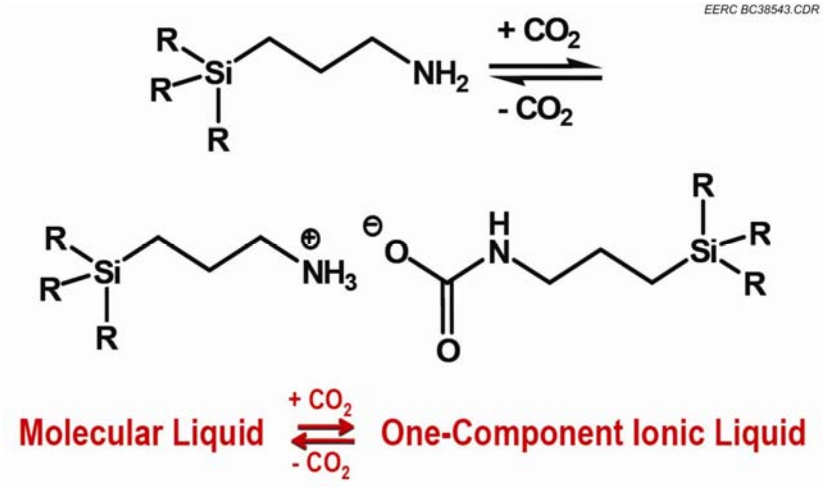


Figure 33. Capture mechanism of a one-component reversible ionic liquid (taken from Eckert, 2009).

Capacity Oligomers for Low-Cost CO_2 Capture." The second is a new ARPA–E-funded project entitled "CO_2 Capture Process Using Phase-Changing Absorbents."

High-Capacity Oligomers for CO_2 Capture

An oligomer is a polymer with relatively few structural units that typically is highly soluble in appropriate solvents. A research program is being conducted by a team of chemists, chemical engineers, and molecular and process modelers from GE Global Research, GE Energy, and the University of Pittsburgh. The program is using molecular modeling to identify suitable candidate oligomers, to synthesize and determine the relevant physical and chemical properties of these compounds, and to model the performance of a power plant integrated with an absorber–stripper postcombustion capture system. Targeted absorbent properties are low volatility, high CO_2-loading capacity, low HR, high reaction rate, high desorption pressure, and low cost (Grocela, 2009). The team has found that that certain amino silicones (some amino silicones serve as one of the active ingredients in hair conditioners) meet these requirements and offer a 50% increase in CO_2-loading capacity when combined in a nonaqueous glycol solvent (Perry 2010a).

CO_2 Capture Process Using Phase-Changing Absorbents

During their work on the high-capacity oligomers, the GE-led team discovered that some amino silicones, when used as a pure component liquid, react with the CO_2 in the flue gas to form a solid (Perry, 2010b). This approach offers the potential to utilize a solution having an increased CO_2 absorption capacity compared to the current cosolvent (amino silicone in glycol) approach (Perry, 2010b). However, it will require a different process flow scheme in order to employ it optimally for postcombustion CO_2 capture. The GE-led team has received funding through ARPA–E to develop a novel, cost-efficient CO_2 capture process that uses the phase-changing absorbent (U.S. Department of Energy Advanced Research Projects Agency – Energy, 2010b). The project goals are <10% parasitic power load at 90% CO_2 capture and <$25/ton CO_2 capture cost. They anticipate that the process will require a smaller footprint than existing postcombustion CO_2 capture processes.

Adsorption

Adsorption is the partitioning of a molecule from a bulk fluid phase to the surface of a solid. Typically, adsorption processes for CO_2 capture include not only "true adsorption," where CO_2 is adsorbed onto the surface of a solid, but also hybrid adsorption processes, where the real mechanism is absorption of CO_2 into a liquid that is supported on or in a solid particle.

Like absorption, the process of adsorption can be physical, where weak attractive forces partition the CO_2 onto the surface and into the pores of a solid, and chemical, where the CO_2 reacts with functional groups on the solid surface to form a bicarbonate, carbonate, or carbamate. The most common reactive functional group for chemical adsorption are metal carbonates, metal oxides, metal hydroxides, or amino groups, the same reactive functional groups that do the work in the solutions used as chemical absorbents.

Solids cannot be pumped from the vessel used to capture the CO_2 from the flue gas to a second vessel in which the purified CO_2 is released and the sorbent regenerated in the same way as a liquid. Therefore, the types of processes used for adsorbent-based CO_2 capture differ from the now-familiar absorber–stripper. The processes that are used can be categorized based on the change made between the CO_2 loading step and the release of CO_2 from the solid as well as the approach taken to contact the gas and the solid. These include:

- Pressure. In PSA, sorbent loading takes place under high-pressure. Pressure is released or a vacuum applied in order to remove the adsorbed gas from the solid and regenerate the adsorbent. Vacuum swing adsorption (VSA) and vacuum pressure swing adsorption (VPSA) are special types of PSA where a vacuum is applied during regeneration.

- Temperature. In temperature swing adsorption (TSA), adsorption takes place at a low temperature. Regeneration of the adsorbent is accomplished by heating the loaded adsorbent, which causes the adsorbed gas to be released.

- Electric current. Electrical swing adsorption (ESA) is effectively a TSA process where heating of the adsorbent is achieved by passing a current through the adsorbent. This type of ESA is really a special type of TSA.

- Combined adsorption–reaction. These are not purely adsorption separation processes but processes where adsorption is used in combination with a chemical reaction to enhance the rate and/or extent of a desired reaction (e.g., sorption-enhanced WGS process). Chemical-looping combustion, discussed in the "During Combustion" section of this report, can be classified as a combined adsorption–reaction separation process where the adsorbent is used to transport oxygen into the combustion reaction chamber.

Traditionally, PSA and TSA are performed in fixed-bed adsorbers. Adsorbers are cyclically operated in adsorption and desorption mode with multiple adsorbers used in series and/or in parallel to permit continuous processing of gas. A series of adsorbers would be used to produce high-quality product gas (or a low-discharge flue gas CO_2 concentration) and to maximize loading of the adsorbent before regeneration. Parallel flow paths would be used to treat high gas flow rates in appropriately sized absorbers and/or to allow cycling of adsorption and regeneration where a single adsorber is used rather than multiple adsorbers in series. Figure 34 illustrates the general steps taken in a fixed-bed PSA system. The diagram shows the product as the gas that is not adsorbed. For precombustion separation applications, both the adsorbed (e.g., CO_2) and not adsorbed (e.g., H_2) gas would be desired as a product. Each fixed bed is cycled through steps that include loading, depressurization, purging, and depressurization. Optimizing the process cycle for removal and purification of CO_2 in PSA is a topic of considerable importance. Some of the recent work published in that area indicates that during precombustion CO_2 capture on shifted syngas, it should be possible to recover 99% pure H_2 while capturing 92% of the CO_2 at 96% purity (Agarwal and others, 2009). Moreover, these cycles can recover more than 92% of the CO_2 with a power consumption as low as 46.8 kWh/tonne CO_2 captured. Other work on PSA cycles for CO_2 capture from flue gas have also indicated a good potential for high-percentage CO_2 capture at high CO_2 purities when using appropriate sorbents and PSA cycles (Reynolds and others, 2005; Ritter, 2004).

Other types of adsorbers include expanded- and fluidized-bed adsorbers where the adsorbent still stays in the same vessel but is not fixed in place. Advantages can be lower pressure drop and low sensitivity to particulate contaminants. The use of fluidized-bed adsorbers also enables operation in a mode where the solids are removed from the adsorption vessel and

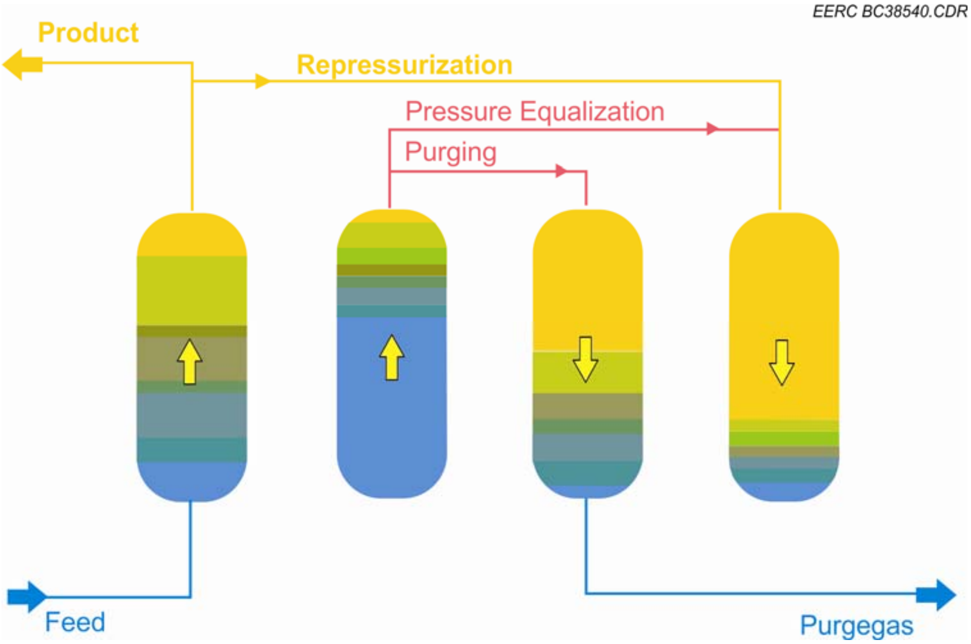


Figure 34. General scheme for PSA (taken from Linde AG, 2010a).

transported to the regeneration vessel analogously to the way that liquid absorbents are transported from the absorber to the stripper. In moving-bed adsorption, the sorbent is entrained in the gas phase and transported to the location where it is separated from the gas phase.

Almost every type of adsorbent discussed has been incorporated into a membrane separation system, usually as a composite polymer membrane containing very-small-particle-size pieces of the solid material within the polymer matrix. Addition of the adsorbent alters the properties of the membrane, helping to either speed the rate of transport of the desired gas or slow the transport of other gases. Work on these composite membranes is discussed in the membrane section of this report.

Table 3 contains a description of NETL's view of the five reactor system types that can be employed for solid sorbents for postcombustion CO_2 capture (Richards, 2009). The reader should note that these are all based on the use of a temperature swing between the adsorption (low-temperature) and regeneration (high-temperature) steps. PSA would be more likely to be applied to precombustion separations.

ADA–Environmental Solutions Adsorbent Screening Study

A DOE-funded project being performed by ADA–Environmental Solutions (ADA–ES) involved the screening of physical and chemical adsorbents. ADA–ES screened over 100 materials classified into four categories: supported amines, carbon, zeolites, and carbonates (Sjostrom, 2010). Figure 35 is a summary of the screening studies in which the sorbent types are compared against MEA with respect to working capacity (how much CO_2 can be captured and released in one cycle per unit of adsorbent) and theoretical regeneration energy (TRE). The three additional classifications given are thermal stability, thermal management, and any special issues that present difficulties for that sorbent type. Green indicates a favorable characteristic, yellow

Table 3. Five Reactor System Types for Use of Solid Sorbents (Richards, 2009)

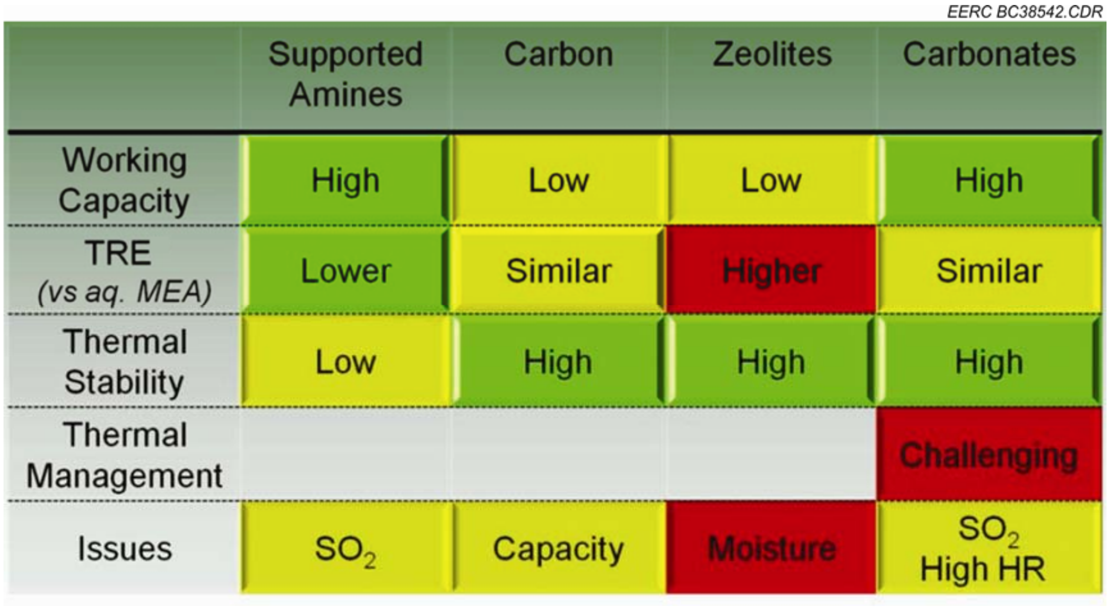
Structured-Bed Concept
- Fixed-bed adsorber, with internal heat removal
- Internal heating of same bed for regeneration

Moving-Bed Concept
- Moving-bed adsorber, with internal heat removal
- Moving-bed regenerator, with internal heating

Fluidized-Bed Concept
- Fluid-bed adsorber, with internal heat removal
- Moving-bed regenerator, with internal heating

Fixed-Bed Adsorber Concept
- Fixed-bed adsorber; adiabatic; multistage with interstage heat removal
- Heating of same bed for regeneration with hot fluid stream

Transport Reactor
- Circulating fluid-bed adsorber
- Circulating fluid- or moving-bed regenerator



	Supported Amines	Carbon	Zeolites	Carbonates
Working Capacity	High	Low	Low	High
TRE *(vs aq. MEA)*	Lower	Similar	Higher	Similar
Thermal Stability	Low	High	High	High
Thermal Management				Challenging
Issues	SO$_2$	Capacity	Moisture	SO$_2$ High HR

Figure 35. Classification of adsorbent types based on ADA–ES screening tests (taken from Sjostrom, 2010).

indicates a characteristic that needs to be managed, and red indicates a characteristic that will make it difficult to engineer a cost-effective solution using this type of system. It should be noted that these rankings are for postcombustion capture. Different sorbents will be useful for precombustion and during-combustion applications than those which are most favorable for postcombustion capture. For example, while it appears from Figure 35 that supported amines may have the most favorable characteristics for postcombustion capture, they would not be useful for capture during combustion and are unlikely to be the best choice for precombustion applications.

ADA–ES has selected the two most promising sorbents for testing in a 1-MW-equivalent slipstream moving-bed contactor it plans to operate at three field sites: Southern Company and Alabama Power's E.C. Gaston Station, Luminant's Martin Lake Station, and an Xcel Energy plant (U.S. Department of Energy National Energy Technology Laboratory, 2009d).

Physical Adsorption (TSA, PSA, and ESA)

Zeolites

Zeolites are microporous aluminosilicate minerals that can occur naturally or be synthesized. They are commonly used as molecular sieves for gas purification and drying. Approximately 40 naturally occurring zeolites have been identified, and over 135 synthetic zeolites have been synthesized. The mineral structure of a zeolite makes it look and behave as molecular cage, as shown in Figure 36. The most common adsorption application for zeolites is

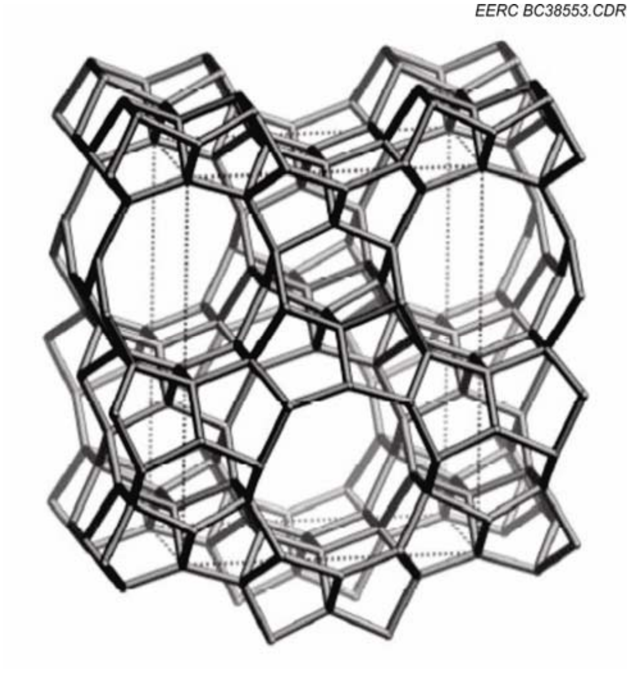


Figure 36. Porous cage structure of zeolite ZSM-5 (taken from Baerlocher and others, 2001).

removal of low concentrations of contaminants. Both pressure swing and temperature swing regeneration are used to remove adsorbed contaminants from zeolites. Some zeolites commonly used for moisture removal chemically react with CO_2 to form carbonates that are not removed in pressure swing applications.

Direct use of true zeolites for carbon capture is possible, but because they tend to have low capacity, their potential for use in postcombustion capture applications has been largely displaced by derivatives that include amine-functionalized zeolites, metal organic frameworks (MOFs) that have similar physical cage structures but contain organic compounds as part of the cage structure, and zeolitic imidazolate frameworks (ZIFs) that might be classified as a special type of MOF. Some MOFs and ZIFs can act as physical absorbents, but with the inclusion of appropriate reactive functional groups, it is possible to get higher-adsorption-capacity MOFs that are chemical adsorbents. MOFs, ZIFs, zeolites that chemically react with CO_2 to form carbonates, and liquid absorbents supported in zeolites are discussed in the section on chemical adsorbents.

Carbon Nanotubes and Activated Carbon

Carbon nanotubes and activated carbon act in a manner similar to zeolites in that small pores act as molecular sieves, preferentially adsorbing molecules of a particular size. Many research groups have investigated activated carbons and carbon nanotubes. The few highlighted here are examples of the work being done that is focused on CO_2 capture. Some research groups have attached reactive functional groups to activated carbons and carbon nanotubes, transforming them into reactive adsorbents. Others have trapped liquid absorbents in the macropores of carbon-based solid supports, creating hybrid or mixed absorption/adsorption media that can be used in adsorption-type process equipment. Much of the work with carbon-based adsorbents involves surface functionalization such that the carbon acts not only as a physical adsorbent but also as a chemical adsorbent. Studies where the researchers have clearly indicated the use of an amine functional group or attached amine are presented in a later section of this report.

Advanced Technology Materials, Inc., and SRI International's Novel Carbon Sorbent

Advanced Technology Materials, Inc. (ATMI) and the SRI International are developing a novel carbon-based CO_2 sorbent with moderate thermal regeneration requirements (80°–100°C) (Hornbostel, 2009). The researchers expect the sorbent to be low-cost, stable, have a low HR for adsorption (25–28 kJ/mole CO_2), and of high CO_2 load capacity (0.1 to 0.2 kg of CO_2 per kg of sorbent (Hornbostel, 2009). The high-surface-area, carbon-based adsorbent will be chemically functionalized in order to increase the selectivity and loading for CO_2 capture and to reduce thermal requirements for CO_2 desorption. The only information available concerning the structure of the sorbent is the image shown in Figure 37. ATMI also markets monolithic carbon adsorbents that are used in the semiconductor industry (Advanced Technology Materials, Inc., 2010).

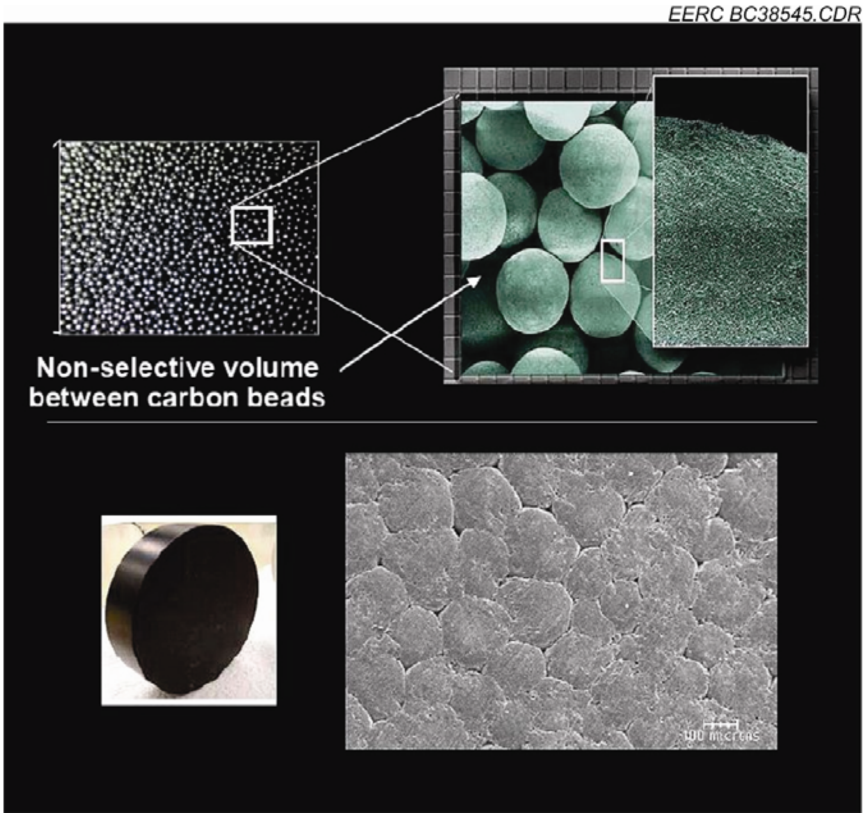


Figure 37. ATMI's adsorbent carbon materials (taken from U.S. Department of Energy National Energy Technology Laboratory, 2009c).

The functionalized carbon adsorbent will be used in a moving-bed adsorber–regenerator, a process similar to that typically used for liquid absorbent-based absorber–strippers and which is shown in Figure 38. The flue gas stream is cooled in a DCC to decrease its temperature to near-ambient conditions. The cooled flue gas from the DCC passes through a moving-bed reactor of carbon sorbent pellets, and CO_2 is absorbed. The CO_2-laden sorbent is transported to a second moving-bed reactor, where it is indirectly heated by steam coils to release the CO_2. Technical challenges with this system include competitive adsorption of moisture and other components in the flue gas, removal of heat during adsorption to maintain a low-temperature environment for the reaction, selection of a bed reactor, and heat exchange between the rich and lean sorbents. The project plans to validate the performance of the carbon-based sorbent concept on a bench-scale system, to perform parametric experiments to determine optimum operating conditions, and to evaluate the technical and economic viability of the technology.

Electrical Swing Adsorption

In the ESA process, an electrically conductive carbon fiber material is used as the support structure for an adsorbent material. This can be a physical adsorbent molecular sieve material such as activated carbon or a zeolite or a chemical adsorbent such as a functionalized activated carbon. The target gas molecules are adsorbed onto the material, which is sometimes referred to as a fixed-bed carbon fiber composite molecular sieve (CFCMS). Regeneration of the sorbent is achieved by passing a low-voltage electrical current through the continuous carbon skeleton. This causes localized heating of the material and thus effects the thermal swing required to desorb the CO_2. An illustration of the seven-step cycle of an ESA system is shown in Figure 39.

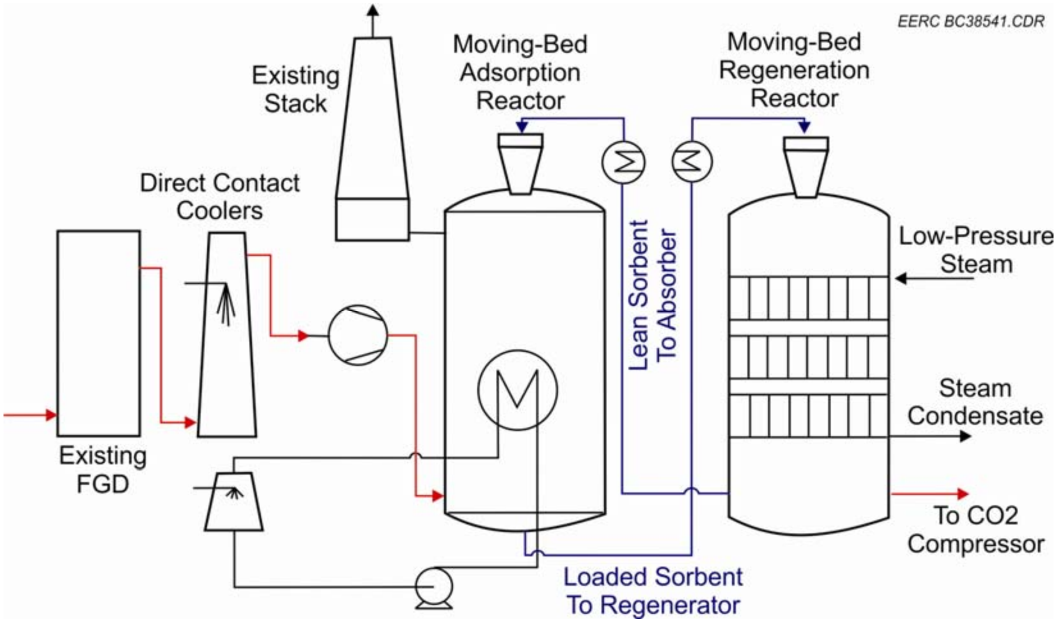


Figure 38. Schematic of SRI International novel carbon sorbent system (taken from Hornbostel, 2009).

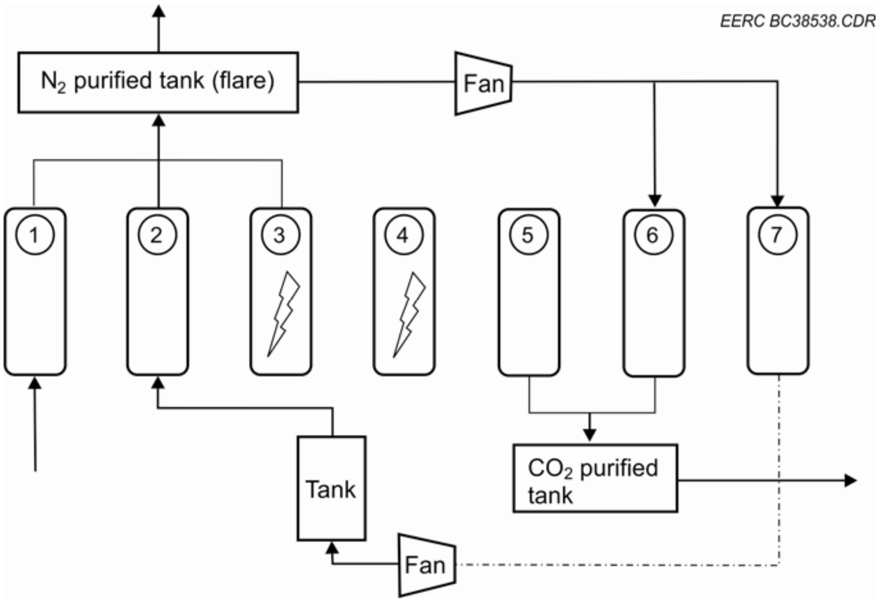


Figure 39. Scheme showing the steps employed in the ESA process to capture CO_2 from flue gases, including 1) feed, 2) rinse with recycled gas, 3) internal rinse, 4) electrification, 5) depressurization, 6) purge, and 7) purge to provide gas for recycle (taken from Grande and others, 2009).

Advertised advantages of ESA over TSA include faster heating (leading to shorter regeneration times and higher unit productivities) and no requirement for sweep gas or steam to carry the heat into the fixed bed so that the adsorbed gas is more easily recovered as an undiluted product. It is easier to achieve a large temperature swing between the low adsorption temperature and the high regeneration temperature, thus maximizing the working capacity of the adsorbent.

Four research groups have published work on the use of ESA for CO_2 capture: CNRS in Nancy, France (Ettlili and others, 2007); ORNL (Baker and others, 2006), the University of Porto, Portugal (Grande and others, 2008, 2009, 2010); and a group at the University of Queensland, St. Lucia, Australia (Ana and others, 2010). None of these efforts has proceeded beyond the use of small lab-scale systems.

The group at ORNL has also investigated the use of ESA for the separation of air into oxygen and nitrogen.

Si/Al Gels

Silicon/alumina gels are the amorphous cousins of the crystalline aluminosilicate zeolites. They also serve as highly porous molecular sieves. Silica gels are finding most of their potential for use in carbon capture not as physical adsorbents but in mixed adsorption/absorption as supports for amines and ionic liquids and in chemical adsorption through attachment of amine functional groups.

Chemical Adsorption

Metal Oxides and Other Minerals

Researchers at NETL have been conducting theoretical modeling studies on the use of metal oxides and metal hydroxides as solid adsorbents for postcombustion CO_2 capture. Through the analysis, sodium and potassium bicarbonate–carbonate pairs ($NaHCO_3$–Na_2CO_3, $KHCO_3$–K_2CO_3) as well as magnesium oxide (MgO) and magnesium hydroxide $Mg(OH)_2$ have been identified as good candidates for use as postcombustion CO_2 adsorbents (Duan, 2010). Another group at NETL has been studying the use of an $Mg(OH)_2$-containing sorbent for precombustion CO_2 capture (Siriwardane and Stevens, 2009; Siriwardane and others, 2007). One advantage to this approach appears to be the ability to perform the adsorption step at an elevated temperature (200°−315°C) that would eliminate the need for the cooling that is required when using physical solvents such as Rectisol in a coal gasification system. Thermodynamic analysis conducted with the FactSage software package indicated that the $Mg(OH)_2$ sorbent system is highly favorable for CO_2 capture at temperatures and pressures up to 400°C and 30 atm. $MgCO_3$ formed during sorption decomposes to release CO_2 at temperatures as low as 375°C with pressures up to 20 atm. The MgO formed after CO_2 release could be converted back to $Mg(OH)_2$ (rehydroxylation) at temperatures up to 300°C at 20 atm. Experimental data confirmed sorbent regeneration at 375°C, and a multicycle test conducted in a high-pressure fixed-bed reactor at 200°C with 28% CO_2 showed stable reactivity during cyclic tests. The potential for use at high pressure and high temperature is particularly advantageous for precombustion capture applications, and the high-pressure regeneration is advantageous because it decreases CO_2 compression costs.

Stabilized Calcium Oxide Adsorbents with Improved Durability for High-Temperature CO_2 Capture

A group at Pacific Northwest National Laboratory (PNNL) has been working with calcium oxide (CaO)-based adsorbents. The stated advantage is that these sorbents can be used at elevated temperatures. Normally, CaO-based absorbents undergo a loss of CO_2 transport capacity over many carbonation–decarbonation cycles because of sintering. In the PNNL work, it was found that mixing CaO precursors with small rodlike $MgAl_2O_4$ spinel nanoparticles provided a CaO-based adsorbent with improved high-temperature durability (Li and others, 2010). The process that was developed created a 34 wt%-CO_2 capacity adsorbent that was found to be stable for over 65 carbonation−decarbonation cycles when carbonation (adsorption) was performed at 650°C and calcination (decarbonation, or regeneration) was performed at 850°C (Li and others, 2010). For comparison, the CO_2 capacity of natural dolomite (which is 35 wt% MgO and 65 wt% CaO) decreased rapidly from 25 wt% for the first cycle to less than 5 wt% for the fiftieth cycle (Li and others, 2010).

RTI International – Dry Sorbent-Based Capture Process

The RTI International high-temperature dry adsorbent-based, postcombustion capture process development program is in the sixth year of NETL sponsorship. Research team members and subcontract partners include RTI International; NETL; EPRI; ARCADIS, Inc.; the U.S. Environmental Protection Agency (EPA); Sud-Chemie, Inc.; and Nexant.

The dry sorbent-based capture process is illustrated in Figure 40. The concept is to use a metal carbonate-based adsorbent that is transformed into a metal bicarbonate in the adsorber and then regenerated through release of CO_2 in the regenerator. The metal carbonate-to-metal bicarbonate swing allows a maximum CO_2 transport of 1 gm of CO_2 for every 2.4 gm of metal (Na) carbonate that is fed to the adsorber each cycle (Nelson and others, 2009).

The adsorber is fed solid sodium carbonate that reacts with water and CO_2 in the flue gas to form solid sodium bicarbonate. This is an exothermic reaction that is performed at lower temperatures, with intercooling to remove the HR. The bicarbonate solid is then transported to the regenerator where heat is added to drive off the CO_2 and water to regenerate the metal carbonate. This is an endothermic reaction performed at higher temperatures, so heat must be added to supply the required energy. A condenser is used to remove water from the CO_2 stream, and the CO_2 is subjected to compression, drying, and if necessary, purification.

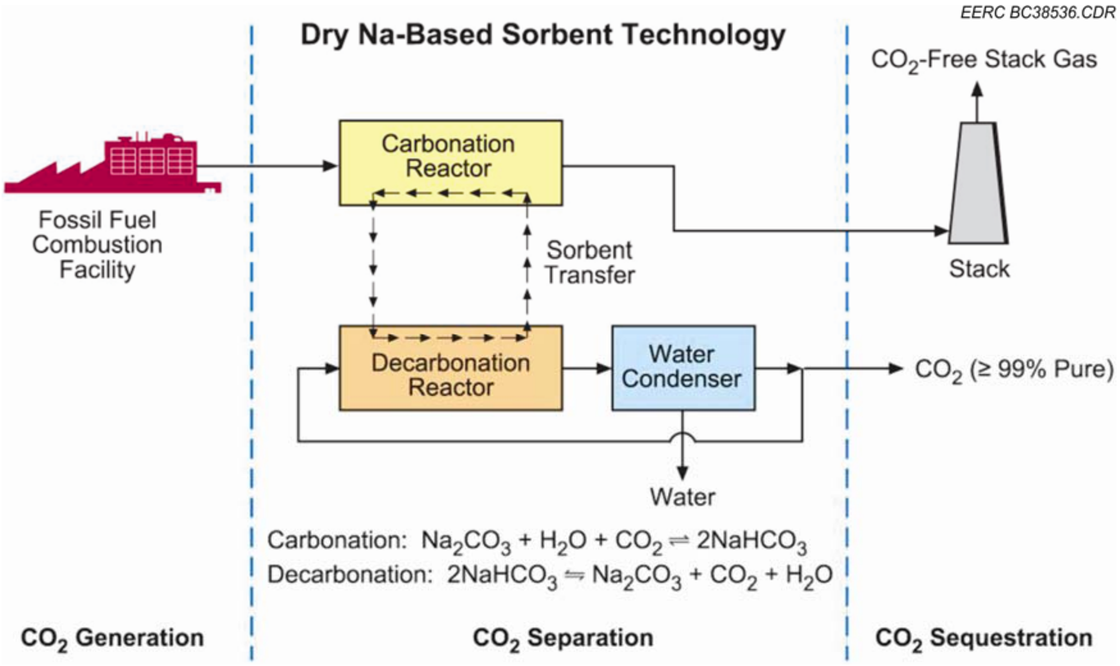


Figure 40. RTI International capture process using dry regenerable sorbent (taken from Gupta, 2004).

Figure 41 is a schematic diagram of the system including a deep sulfur scrubber, a downflow cocurrent adsorber, the steam-jacketed screw conveyer used for regeneration and production of the purified CO_2 gas stream, and the cooling-water-jacketed screw conveyer used to move the sorbent back to the adsorber.

There are many advantages to the process, including low regeneration energy requirements relative to amines, production of essentially pure CO_2, and compatibility with current power plant operating conditions. Challenges include the need for efficient heat removal to prevent self-extinguishing of the reaction, continuous circulation of solids, and the fact that the sorbent reacts with other contaminants such as SO_2 and particulate (Nelson and others, 2009).

Both the sorbent and the process have been tested with natural gas and coal-fired flue gas at EPA's multipollutant control research facility (MPCRF). The system was operated for 130 hr on natural gas-derived flue gas containing approximately 6 vol% CO_2. The maximum CO_2removal achieved was roughly 99%. When operated on coal-derived flue gas for 105 hr at a CO_2 concentration of about 10.5 vol% and a SO_2 concentration of roughly 20 ppm (mixture of eastern bituminous and Powder River Basin subbituminous coals), the maximum CO_2 removal was approximately 92% (Nelson and others, 2009).

Current work involves scaling up to a 1-ton/day CO_2 capture system, with the sorbent manufacturing partner Sud-Chemie, Inc., scaling its manufacturing capacity sufficient to provide for that demonstration and planning for production of sufficient material for a 100-ton/day

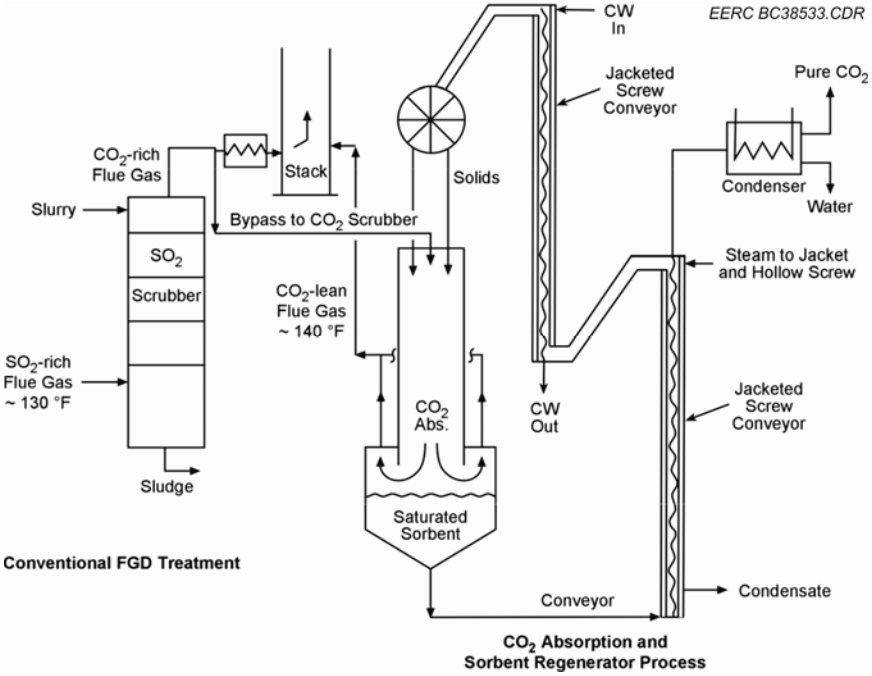


Figure 41. Dry carbonate process (taken from Nelson and others, 2008).

system by 2012. The target date for technology commercialization is 2015 (Nelson and others, 2009).

Regenerable Magnesium Oxide-Based Adsorbents

A group at the Illinois Institute of Technology and GTI developed regenerable MgO-based adsorbents for use in capture of CO_2 from raw syngas (Abbasian and others, 2005). The magnesium-based sorbents were found to be useful over a temperature range of 300°–450°C and at a pressure of 20 atm. CO_2 adsorption through carbonation of the MgO occurs at gasification process conditions, with sorbent regeneration being carried out by increasing the temperature to produce a concentrated stream of CO_2. The sorbents were prepared from dolomite (a type of limestone). Partial calcinations and impregnation with potassium salts helped produce a mechanically stable and highly reactive sorbent (Hassanzadeh and Abbasian, 2010). Tests found that generation temperature greater than 425°C required a heat source other than waste heat and that the reactivity gradually decreased during the sorption–regeneration cycles.

Sorption-Enhanced Water–Gas Shift (SEWGS) Process

The SEWGS process developed by Air Products and Chemicals, BP, and Energy Research Centre of the Netherlands combines the use of a potassium-promoted hydrotalcite-based CO_2 sorbent and a commercial iron–chromium shift catalyst (van Selow and others, 2009). Hydrotalcite is an anionic clay mineral that has found use as an antacid. It is a secondary mineral in the ultramafic rock serpentinite, one of the high magnesium-content rocks viewed as a potential resource for use in accelerated weathering-based CO_2 capture. The sorption process involves formation of $MgCO_3$. Sorbent regeneration occurs by stripping with low-pressure steam at about 400°C (van Selow and others, 2008). In the process, multiple adiabatic fixed beds cycle between the shift reaction with adsorption and regeneration steps. Removal of CO_2 during the shift reaction removes the normal equilibrium barrier presented by accumulation of CO_2 in the normal shift process, thus increasing the conversion efficiency.

SEWGS is capable of capturing more than 90% of the CO_2 while producing a very pure CO_2 stream (Allam and others, 2004). The process shows promise for use in hydrogen production and IGCC applications Cobden and others (2007). The SEWGS process has not yet been commercialized but has been scaled to a large laboratory/pilot-scale, four-bed multicolumn system as part of CACHET, a 3-year, integrated research project funded by the European Commission and the international industrial/governmental CO_2 Capture Project (CCP). Further development and testing are under way, with large-scale pilot testing planned for the near future (Energieonderzoek Centrum Nederland, 2010). Some of the other key references describing development of SEWGS include those by Allam and others (2005) and Hufton and others (2006).

Metal Organic Frameworks

MOFs are organic compound-containing cage structures. With the appropriate selection of the organic and inorganic components, a self-assembling MOF is formed with engineered macromolecular cavities that can act as sites for physical and/or chemical adsorption of CO_2.

MOFs could be applied to both precombustion and postcombustion capture. Figure 42 shows some examples of the wide variety of MOF structures that have been built. It is apparent that MOFs have pore and cage structures that are similar to zeolites, but because organic compounds serve as part of the pore structure, a greater variety of pore sizes, cage structures, and inclusion of reactive functional groups can be achieved than is possible with the inorganic zeolites. The structures that have been built include examples with surface areas as high as 10,400 m^2/gram and CO_2 storage capacities as high as 2.870 grams of CO_2 per gram of MOF (Furukawa and others, 2010). While having very high capacities is helpful, it is also desirable for a MOF to exhibit fast adsorption and desorption rates. This can be accomplished by building MOFs with pore structures that are a combination of larger and smaller pore sizes. Considerable attention is also being paid to temperature and steam stability of MOFs (Benin and others, 2009). The most likely process application for MOFs is in fixed-bed VPSA for postcombustion CO_2 capture.

While many research groups have published work in the area of MOF development, the leading activities are being performed include 1) a large DOE-funded project managed by UOP and 2) work at University of California Los Angeles and South Korea's Hydrogen Energy R&D Center funded by BASF, the DOE Office of Basic Energy Sciences, and South Korea's Ministry of Education. The UOP project includes research groups at UOP, the University of Michigan, Northwestern University, Vanderbilt University, and the University of Edinburgh.

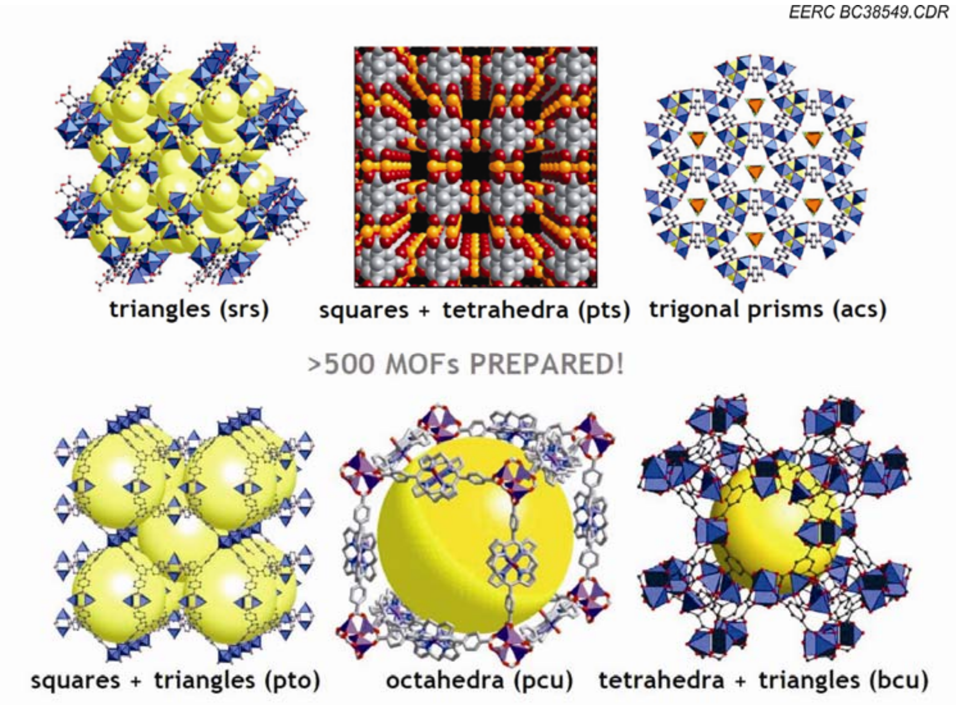


Figure 42. Examples of MOF structures (taken from Yaghi, 2006).

Additional information about MOFs can be found in the fact sheet for the NETL-funded project "CO_2 Removal from Flue Gas Using Microporous Metal Organic Frameworks" (U.S. Department of Energy National Energy Technology Laboratory, 2010b) as well as in Willis and others (2007) and Yazaydin and others (2009).

Zeolitic Imidazolate Framework

ZIFs can be thought of as a special type of MOFs. They are a class of crystalline nanoporous materials made of zeolite minerals and imidazoles at the organic linkages (imidazole's are also used as ionic liquids and for making poly[ionic liquid] polymers). Researchers at PNNL (Nune and others, 2010) and the University of Pittsburgh (Rankin and others, 2009) are developing and testing ZIFs for CO_2 capture. The work appears to be in the early laboratory stage, with a focus on molecular modeling and synthesis of new materials.

TDA Dry Solid Sorbent

TDA Research, Babcock & Wilcox, Louisiana State University, and Western Research Institute are developing a process that uses an alkalized alumina adsorbent to capture CO_2 at intermediate-temperature and near-ambient pressure. The physical adsorbent is regenerated with low-pressure steam. The target adsorption gas–solid contact time is approximately 1.5 seconds, and the target regeneration contact time is 1.5 minutes (Elliot and Srinivas, 2009). Results from system modeling indicate that the TDA dry solid sorbent system with compression should achieve a power loss of 20.7%, where the theoretical minimum is 13.46%. Additional information is available in the project fact sheet (U.S. Department of Energy National Energy Technology Laboratory, 2010d).

Novel Amine-Enriched Solid Sorbents

This technology was developed by NETL and is currently at the laboratory scale. The sorbent consists of a carbon material with amine compounds fixed upon it. When exposed to a CO_2-rich stream, the amine sites react with the CO_2. Temperature swing is used to release the CO_2. High sorption capacities on the order of 4 moles CO_2/kg solid sorbent have been observed. The use of tertiary amines requires lower energy for CO_2 capture when compared with aqueous amine absorbents. When compared to an aqueous solution, the solid has a low heat capacity, and there is a smaller difference between adsorption and regeneration temperatures, meaning that the regeneration energy requirement is low compared to that of MEA (783 Btu/lb CO_2 and 1934 Btu/lb CO_2, respectively) (Pennline and others, 2009; Tarka and Ciferno, 2005).

Comparison of Amine-Functionalized Carbon Nanotubes, Granular Activated Carbon, and Zeolites

Lu and others at National Chung Hsing University, National Chiao Tung University, and Industrial Technology Research Institute in Taiwan reported that amine functionalization of carbon nanotubes provided greater enhancement of adsorption capacity than the same functionalization on activated carbon or zeolites (Lu and others, 2008). Although the researchers expected to see evidence of chemical adsorption because of the amine functional groups, the results suggested that physical adsorption is the principal mechanism. This would lead to a low energy of desorption. The work is in early laboratory phase, and current efforts are focused on investigating the reversibility of CO_2 adsorption by these adsorbents.

Metal Monolithic Amine-Grafted Zeolites

The University of Akron and NETL have been working together to develop a CO_2 capture system that involves the novel integration of a metal monolith containing gas flow channels that have amine-grafted zeolites plated to the walls and heat-transfer fluid flow channels that are used for cooling during CO_2 adsorption and heating during regeneration. Figure 43 summarizes the approach. The metal monolith adsorber works like a specialized fixed-bed adsorber with a very low pressure drop for gas flow and good heat-transfer characteristics for fast heating and cooling during the transition between the adsorption and regeneration steps.

It is expected that the low cost of raw materials for the synthesis of zeolite-grafted amine sorbents combined with the innovative application of metal monoliths as an adsorber structure may lead to a breakthrough technology for the effective capture of CO_2 from flue gas of coal-fired power plants. Additional information is available in the project fact sheet entitled "Metal Monolithic Amine-Grafted Zeolites for CO_2 Capture" (U.S. Department of Energy National Energy Technology Laboratory, 2010e).

University of Ottawa – Recyclable CO_2 Adsorbent

Researchers at the University of Ottawa have developed recyclable CO_2 adsorbents based on surface-modified expanded mesoporous silica (Franchi and others, 2005; Belmabkhouta and others, 2010). The materials exhibit a high adsorption capacity that is both fast and reversible. The adsorbents can be used with both wet and dry gas streams. The most current research paper (Belmabkhouta and others, 2010) indicates the use of the adsorbent to remove CO_2 from air. The use of these adsorbents for CO_2 capture from flue gas has been licensed to Carbon Capture Technologies, Inc., a branch of CSMG Technologies, Inc.

Hyperbranched Aminosilica

HAS adsorbents are chemical adsorbents created by polymerization of hyperbranched amines onto a mesoporous silica substrate. Researchers at Georgia Tech and NETL have succeeded in making several different examples of these materials with different polymeric amines and different mesoporous silicates (Gray and others, 2010; Choi and others, 2009; Hicks and others, 2008; Drese and others, 2009). Good CO_2 adsorption and regeneration behavior has been obtained over temperature ranges of 50°–75°C and 100°–120°C, respectively (Environmental Protection Online, 2008). Performance was stable over multiple cycles, and the adsorbents exhibited a low sensitivity to moisture. Loss of the amine from the surface is not a problem with these adsorbents because the amine polymer is covalently bonded to the solid silica substrate (Hicks and others, 2008).

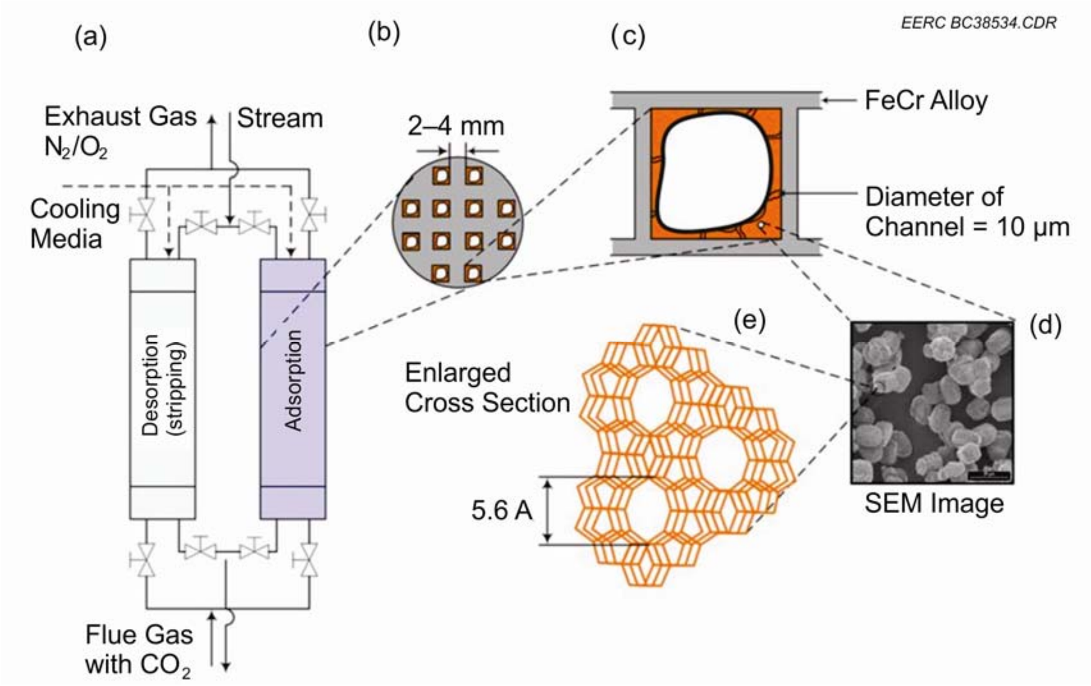


Figure 43. CO_2 capture unit with metal monolithic amine-grafted zeolites (taken from Chuang, 2009).

Other groups involved in working with amine-functionalized silica include Liu and others (2010) in Taiwan, Pirngruber and others (2009) in France, and Zheng and others (2005) at PNNL. Recently, a group in China reported on amine group-containing ionic liquids immobilized to porous silicate solids (Zhang and others, 2009). All of these projects are at the small laboratory scale and are focused on developing adsorbents with favorable characteristics.

Membranes

A membrane is a structure that has lateral dimensions much greater than its thickness through which mass transfer may occur under a variety of driving forces (Koros and others, 1996). Membrane-based gas separations used in carbon capture include those designed to provide separation of oxygen from air for use in oxycombustion and gasification (precombustion), those designed for use in precombustion applications including hydrogen transport membranes and CO_2-permeable membranes, and those used to perform separations of postcombustion flue gas; these are primarily CO_2-permeable membranes. It should be noted that gas-permeable membranes are used commercially for treatment of natural gas in order to upgrade it to pipeline quality, but these applications rarely capture the CO_2 as a purified product. Membranes can also be used as a means of providing gas–liquid contact in place of absorption and/or stripping towers in a much smaller-volume device because of the very high surface area per unit volume. This application was discussed in the "Use of Mass Transfer Devices Other Than Absorption Towers" section of this report.

Gas separation membranes use partial pressure as the driving force for transport. Differences in the ease of transport of the various gas components provide the means for separation. Because the partial pressure difference from the source side of the membrane to the permeate side of the membrane is the driving force, it is easier to transport a selected gas component when the source gas is at a high total pressure and that component is at a high concentration. However, this situation cannot be present at all locations in a membrane separation process if the requirement is removal of most of that component from the feed gas (e.g., capture of 90% of the CO_2) and collection of that component as a purified product (e.g., production of >95% pure CO_2). Separation is achieved because differences in physical and/or chemical interactions between the components present in a gas mixture with the membrane material cause one component to permeate through the membrane faster than the other component(s). The gas component with the highest solubility, fastest diffusion rate, or the ability to ionize or otherwise interact with membrane components under the process conditions is preferentially transported across the membrane.

Figure 44 illustrates the four areas of work involved in development of a new membrane technology. These are development of the membrane material (advanced materials) with an understanding of the basis for its performance including the chemistry and structure (micromorphology), the development of the appropriate physical device (or module) and the ability to make that device (module manufacture), and the design of the process system in which to use that device (system development and modeling). These are shown together in the figure because they are linked efforts that must be performed in concert.

Figure 45 is a representation of general types of membranes (Cowan, 2008). The figure shows several types of polymer membranes, two types of liquid membranes, two types of membrane structures, and lists other types of materials used as membranes. It does not provide a comprehensive list but rather illustrates the diversity. The types of selective processes that occur in these membranes are illustrated in Figure 46. It should be noted that more than one of these selective processes can be involved in one membrane, especially if that membrane is a composite, matrix composite, or liquid membrane. It should not be assumed that metal, ceramic, or zeolite membranes cannot have complex structures or multiple selective processes. Finally, while the basic format of all membranes is essentially a flat sheet or a tube, there is great variety as to how these are packaged into membrane modules. Flat-sheet membranes can be used in plate-and-frame-type modules or in a variety of spiral-wound module designs. Tubular membranes (e.g., hollow-fiber membranes) are typically used to construct modules with epoxy-sealed tube sheets where the source gas flows through the inside of the tube and the permeate is collected from the shell side (or vice-versa).

Gas flow paths in membrane modules generally follow one of four configurations, illustrated in Figure 47. The feed gas is the mixed-gas stream that must be treated or separated. The retentate gas is the effluent-treated feed gas that lost the components that passed through the membrane. The permeate is the effluent gas that includes the gas molecules that passed through the membrane as well as any sweep gas fed to that side of the membrane to act as a diluent (in order to maintain a low partial pressure for the transported gas). Ideally for postcombustion carbon capture, the feed gas (green) is a mixture of nitrogen (blue) and CO_2 (yellow), and it could be separated in one step without the use of a sweep gas (red). Realistically, it will require multiple processing steps and/or the use of a sweep gas that can easily be separated from the CO_2 (e.g., water vapor, which can be separated by condensation through cooling and compression).

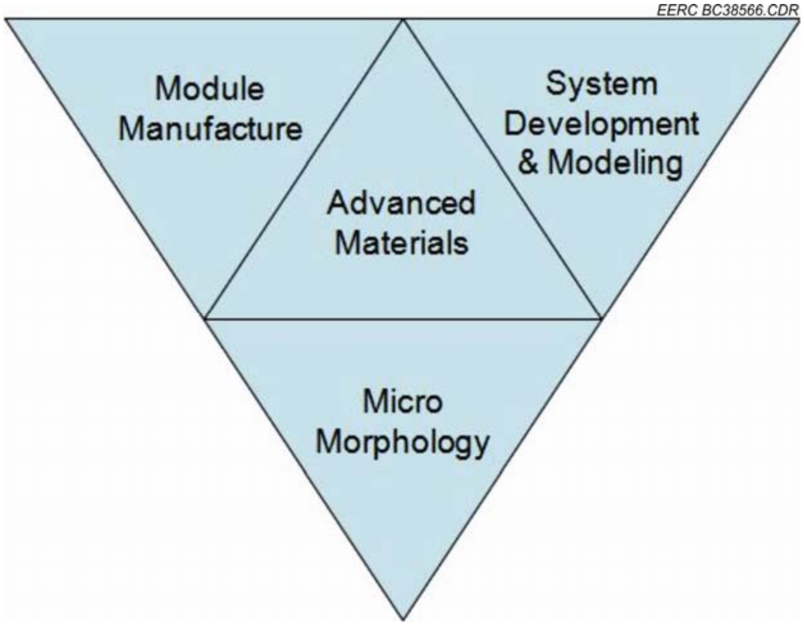


Figure 44. Work required to develop membrane separation technologies (adapted from Koros, 2008).

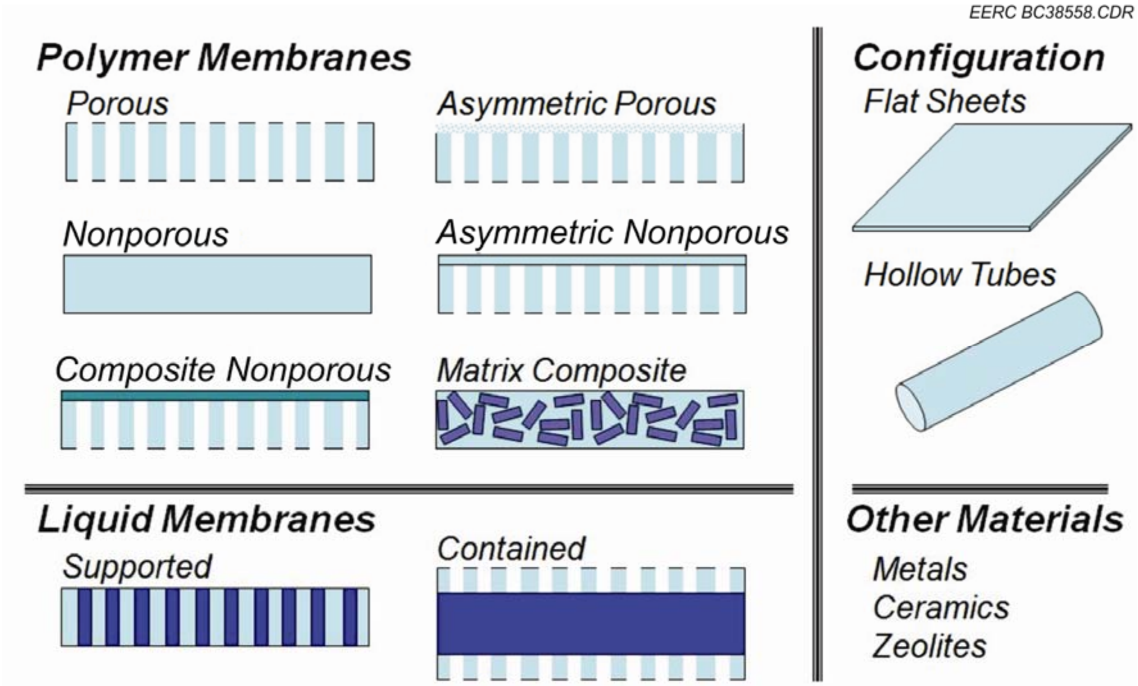


Figure 45. Types of membranes used in separations (taken from Cowan, 2008).

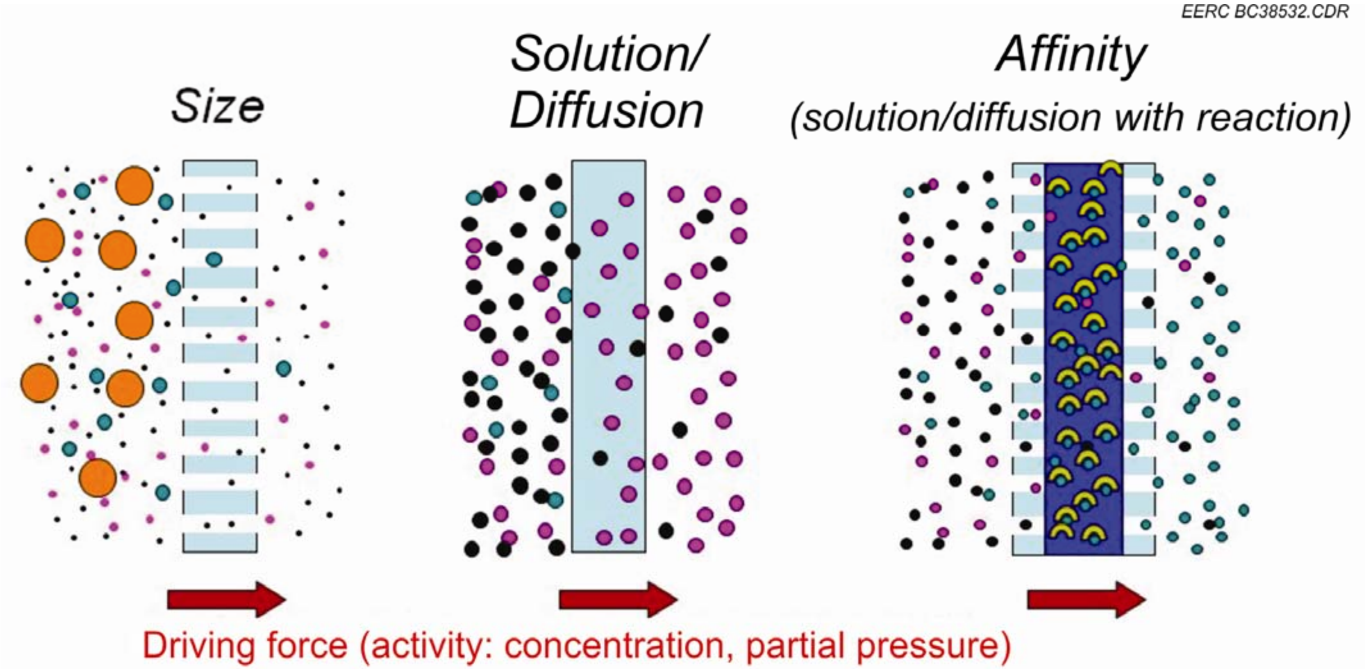


Figure 46. Separation behavior in membranes (taken from Cowan, 2008).

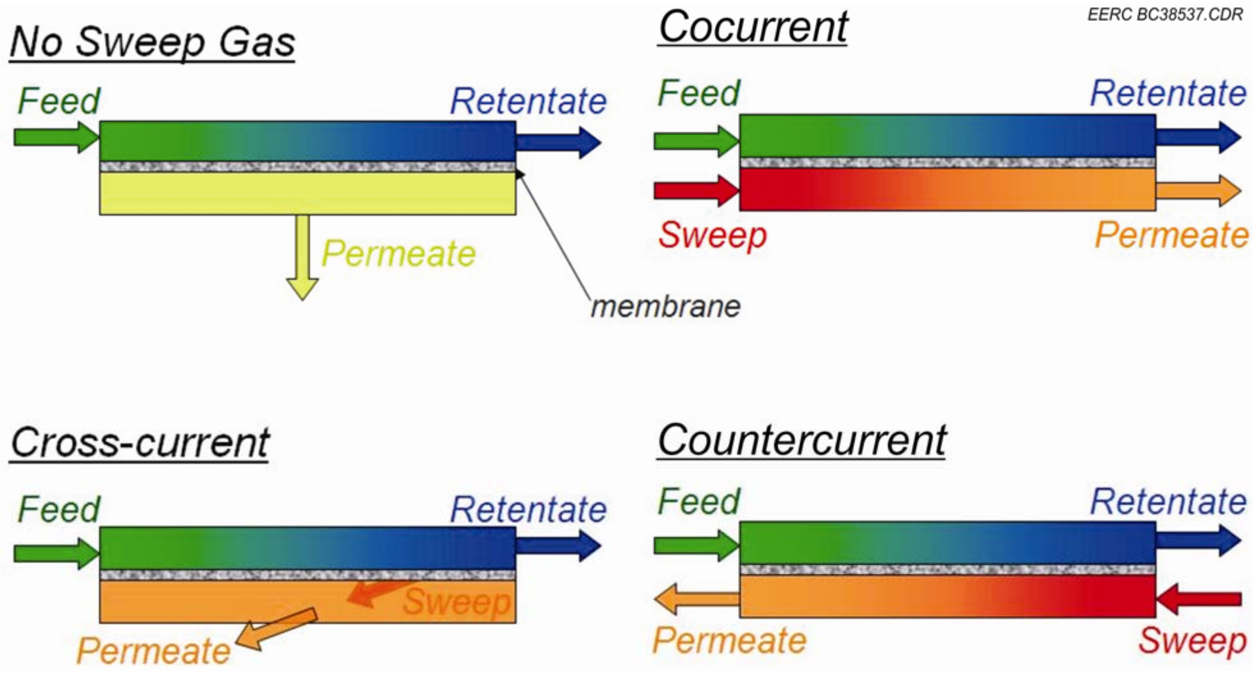


Figure 47. Gas flow paths in membrane modules (taken from Cowan, 2008).

The quality of the separation is determined by the membrane selectivity and by two process parameters: 1) the ratio of the permeate flow to the feed flow, and 2) the ratio of permeate pressure to the feed pressure. Depending upon the selectivity of the membrane, a high-purity CO_2 product may require a large number of stages, leading to increased recompression and capital costs. Membrane separation often competes with cryogenic separation and PSA when medium quantities of low-purity product gas are required. Membrane separation technology is currently better suited to treatment of mixed-gas streams fed from a high-pressure source, such as natural gas processing.

Air Separation for Oxycombustion and Gasification

The traditional method used to obtain a high-volume supply of purified oxygen for oxycombustion and gasification is to perform cryogenic distillation of air in an ASU. This is an energy-intensive process that is likely to represent up to 58% of the parasitic energy load of an oxycombustion carbon capture process (Varagani and others, 2005). Membrane separation techniques are being developed as potential lower-energy replacements for cryogenic ASUs.

Oxygen-Permeable Membranes

Air Products – Ion Transport Membrane

Air Products and Chemicals, with financial assistance over several years from DOE, has developed an ion transport membrane (ITM) oxygen purification system (Shelley, 2009). This system is considered to be at near-commercial stage. It has been demonstrated in a 5-ton/day pilot plant since 2006 and Air Products is currently working on a 150-ton/day test facility with NETL. Air Products hopes to offer a small commercial-scale unit having a capacity of less than 800 tons/day by 2011 and to be operating a full commercial-scale test facility capable of producing 2000 tons/day of oxygen by 2013. Details on the process can be found in the DOE project fact sheet (U.S. Department of Energy National Energy Technology Laboratory, 2009b) or an Air Products online brochure (Air Products and Chemicals, 2008).

Oxygen-Selective Polymer Membranes

Most polymers are either more permeable to oxygen over nitrogen or to nitrogen over oxygen, meaning that the potential exists for development of a polymer membrane-based system for purifying oxygen. Unfortunately, such a system has not yet been developed for the generation of large quantities of pure oxygen from air. Commercial systems can be purchased for membrane-based production of 50% O_2 (Grasys, 2010), and several companies offer membrane-based nitrogen purifiers that generate high-purity nitrogen from air. Polymer membranes containing molecular sieves do show some promise for providing higher-purity oxygen from air. The matrix composite polymer membranes that have been investigated for oxygen purification include polymer membranes utilizing activated carbon (Jones and Koros, 1994; Kusworo and others, 2010) or zeolites (Wang and others, 2002) as the molecular sieve.

Hydrogen Separation and Integrated Precombustion Capture Systems

CO_2-Selective Ceramic Membrane for WGS Reactions

Between 2000 and 2005, DOE funded work by Media and Process Technology, Inc., the University of Southern California, and NETL on the development of a CO_2-selective ceramic membrane for WGS reactions with recovery of CO_2. These membranes were developed for use in a high-temperature membrane reactor (MR) designed to enhance the performance of the WGS reaction through removal and capture of CO_2. Two membranes were developed and tested: a Mg-Al-CO_3-layered double hydroxide (LDH) membrane and a carbonaceous membrane. A hybrid adsorption membrane reactor (HAMR) was also developed that provided close to 100% CO conversion, a high-purity H_2 product fuel, and a concentrated CO_2 product. The HAMR used the LDH as a particulate adsorbent and required off-line regeneration (Liu, 2005).

The tubular ceramic membranes used in the MR and HAMR are made of a porous ceramic that has had its pores filled with hydrotalcite, making them impermeable to all the gases present except CO_2. The membrane tubes are filled with shift catalyst, which converts the CO and water in the syngas to CO_2 and H_2. CO_2 permeates through the hydrotalcite on the membrane, driving further conversion of CO. This technology can be applied to syngas produced from coal gasification. Advantages include a permeate stream that is essentially pure CO_2; a H_2 stream that is maintained at near-syngas-generation pressures; the fact that the fuel gas stream contains both H_2 and water (which is advantageous because additional mass flow from water through the turbine improves power production and efficiency); and a process that operates in the conventional WGS temperature range of 300° to 600°C. Unfortunately, it is difficult to produce defect-free membranes (Liu, 2005).

A mathematical model was developed to simulate the HAMR, and a laboratory-scale reactor was constructed and operated to corroborate the model results. The project was successful in demonstrating enhanced WGS efficiency for hydrogen production with concomitant CO_2 capture (Liu, 2005).

Combined Use of Oxygen Transport Membranes and Hydrogen Transport Membranes for Carbon Capture in Natural Gas Reforming and Coal Gasification

Three membrane technologies developed by Eltron Research and Technology (ERT) are included here: an oxygen transport membrane used to separate oxygen from air; a catalytic membrane reactor (CMR) that serves as both an oxygen transport membrane and a catalytic layer for in situ partial oxidation reforming of methane; and a dense metal alloy membrane for hydrogen separation from the CO_2 and H_2O present in the shifted syngas. All three of these technologies were developed with support from DOE and are discussed in a paper by Mundschau and others (2006).

The oxygen transport membrane operates by dissociating oxygen molecules at the reducing surface of the membrane. The oxygen ions are then transported across the ceramic membrane and converted back to oxygen gas at the oxidizing surface. Electrons flow in the opposite direction through the membrane, forming an electrochemical device that requires no electrical energy input. The driving force is the oxygen partial pressure difference across the membrane, rather than the absolute pressure on each side. Only oxygen from the air side passes through the membrane because only oxygen ions are mobile within the ceramic. No other gases, including carbon monoxide, nitrogen, argon, and methane, are able to pass through the membrane (Eltron, 2009b). Figure 48 is a schematic of the oxygen transport membrane.

The CMR is made from a layer of a ceramic oxide material with a perovskite crystal structure onto which methane steam-reforming catalysts (including noble metal catalysts) are dispersed, a dense perovskite layer that is essentially completely selective toward oxygen, and a support layer. Figure 49 contains a schematic representation of the CMR (top) and photomicrograph of the oxygen-permeable catalytic membrane (bottom). The membrane operates at high temperatures ranging from 850° to 1000°C. Tests on the tubular membranes were performed continuously for up to 9 months under reaction conditions with differential pressures of 250 psi (17.2 bar). The Perovskite materials were found to be stable under the test conditions (Eltron, 2009c).

The dense metal alloy membrane used for H_2 separation has a layer of hydrogen dissociation catalyst on the feed side of the membrane and a catalyst that reduces dissociated hydrogen back to molecular H_2 on the other side of the membrane. Hydrogen partial pressure serves as the driving force to move H_2 across the membrane in dissociated form. Pure H_2 is produced on one side of the membrane and a high-pressure stream of CO_2 and steam with a small amount of CO is produced on the other. Sweep gas can be used for direct injection of the H_2 stream into a hydrogen turbine. When pure H_2 production is desired, no sweep gas is employed (Eltron, 2009a). Figure 50 is a schematic of the dense metal alloy hydrogen separation membrane.

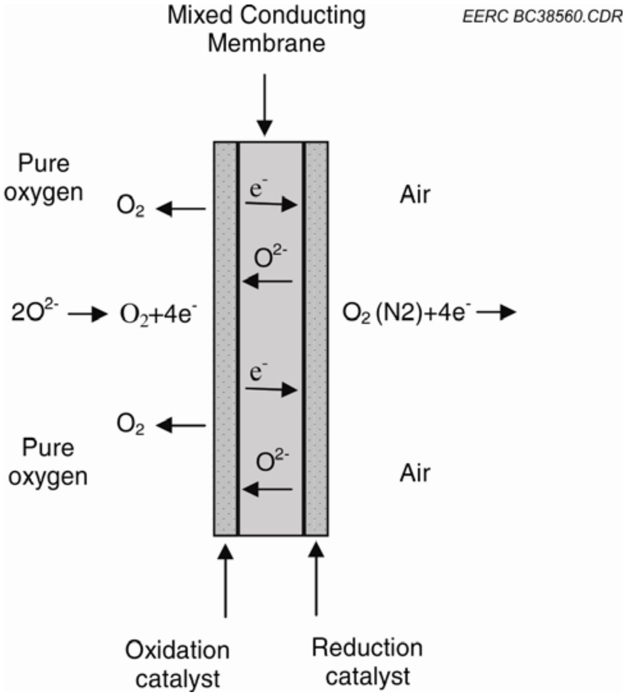


Figure 48. Eltron’s oxygen transport membrane (taken from Eltron, 2009b).

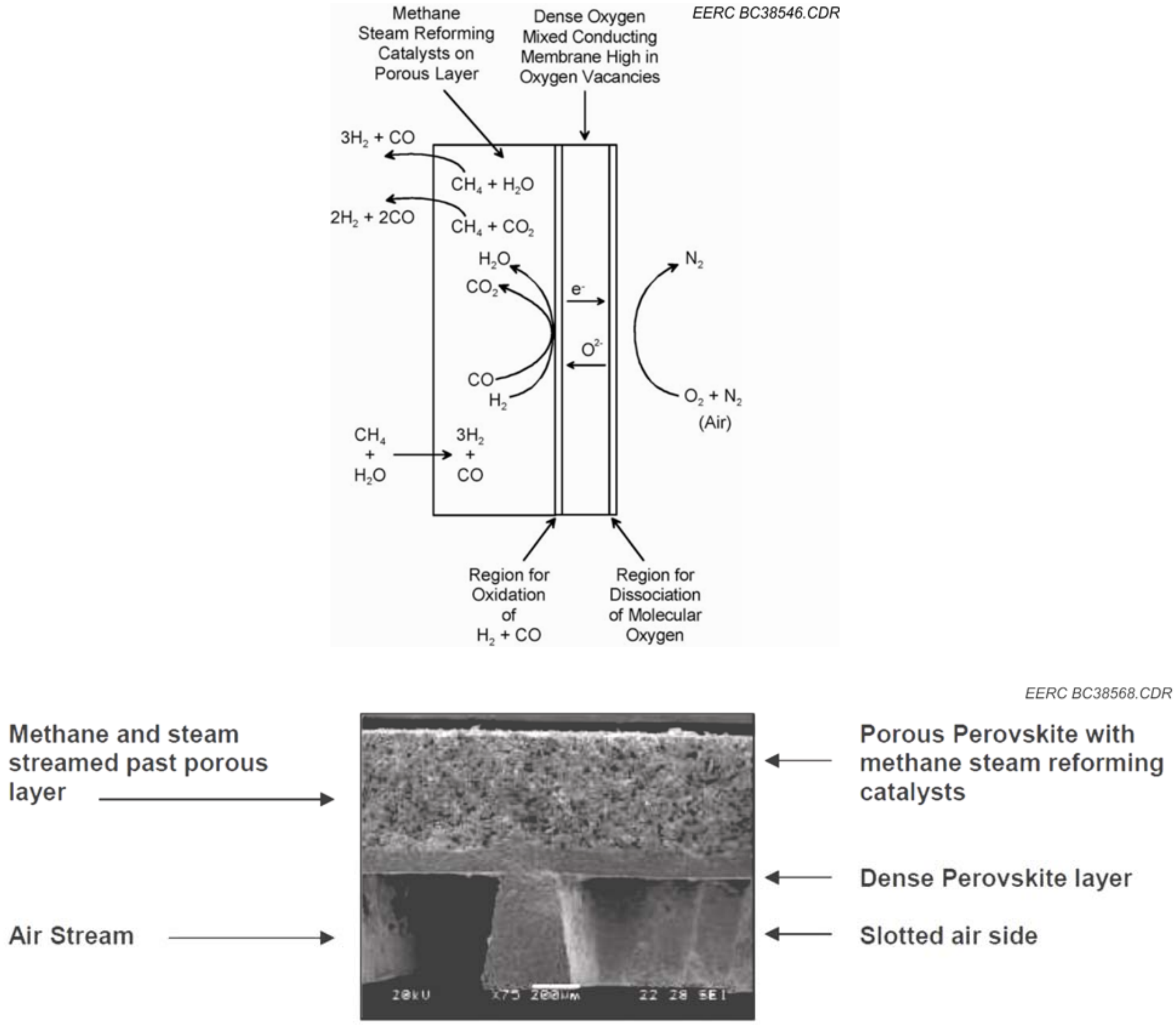


Figure 49. Schematic of catalytic membrane reactor with oxygen transport membrane (top) (taken from Mundschau, et al., 2006) and photomicrograph of the oxygen-permeable CMR (bottom) (taken from Eltron, 2009c).

Palladium-Based Membrane Reactors

Several groups have been developing palladium-based membranes for use in precombustion CO_2 capture. These membranes have catalytic activity for the WGS reaction and are permeable to hydrogen.

Palladium–Copper Alloy Membrane Reactor

NETL and the Colorado School of Mines (CSM) developed a palladium–copper alloy membrane reactor for simultaneous catalysis of the WGS reaction and transport of H_2 across the

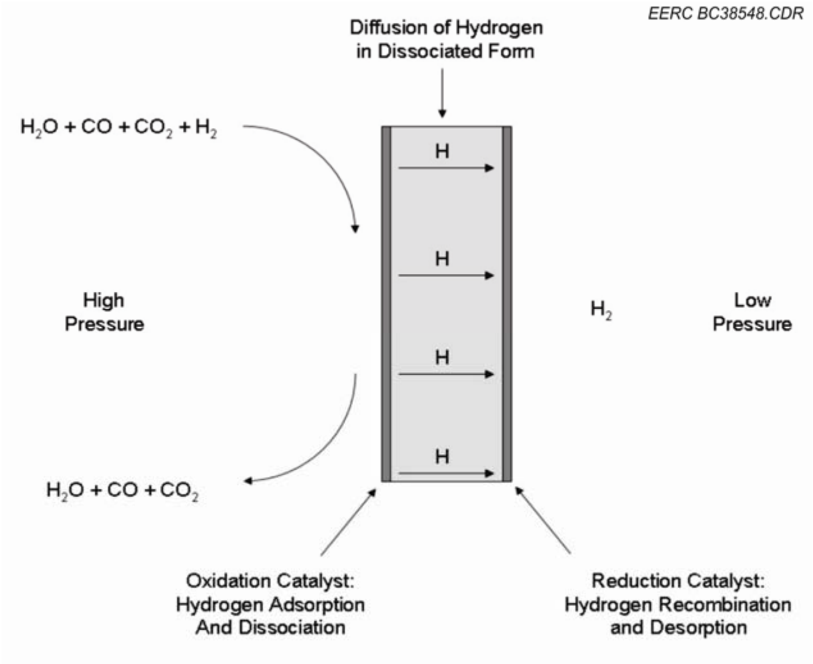


Figure 50. Eltron's hydrogen transport membrane (taken from Eltron, 2009a).

membrane (Romanosky and others, 2007; Way and Thoen, 2006). The high temperature (900°C, 1652°F) and pressure of operation and the catalytic effect of the membrane eliminate the need for a separate WGS catalyst. The palladium–copper alloys are resistant to H_2S degradation.

Hydrogen Membrane Reformer (HMR)

The HMR gas power cycle is a precombustion carbon capture technology under development by StatoilHydro. The HMR technology centers on a syngas reactor that is based on a hydrogen-selective membrane. The reactor combines steam reforming, WGS reaction, and H_2 separation. The reactor utilizes a dense MCM, which is a palladium/silver-based membrane with theoretical infinite selectivity to H_2 permeation. Figure 51 illustrates the process of the cycle. On the feed side of the membrane in the reactor, natural gas or fuel gas is contacted with steam in the presence of reforming catalyst to produce syngas. CO remaining in the syngas after combustion is shifted in downstream shift reactors. A limited amount of air is supplied to the permeate side of the membrane to combust all of the hydrogen that has passed through the membrane, generating "CO_2-free" heat for the endothermic steam–methane reactions. Supplementary CO_2 removal following the WGS reaction is achieved by using a conventional absorption process (Smith and others, 2009).

The HMR reactor has been scaled up to a small-scale, square-channel, monolithic membrane reactor depicted in Figure 52. A complete module is made of the monolith and two manifolds at the ends. The monolith has porous walls and serves as a mechanical support for the thin (30–50-µm) membrane, which is coated in every second channel. A full-scale reactor has

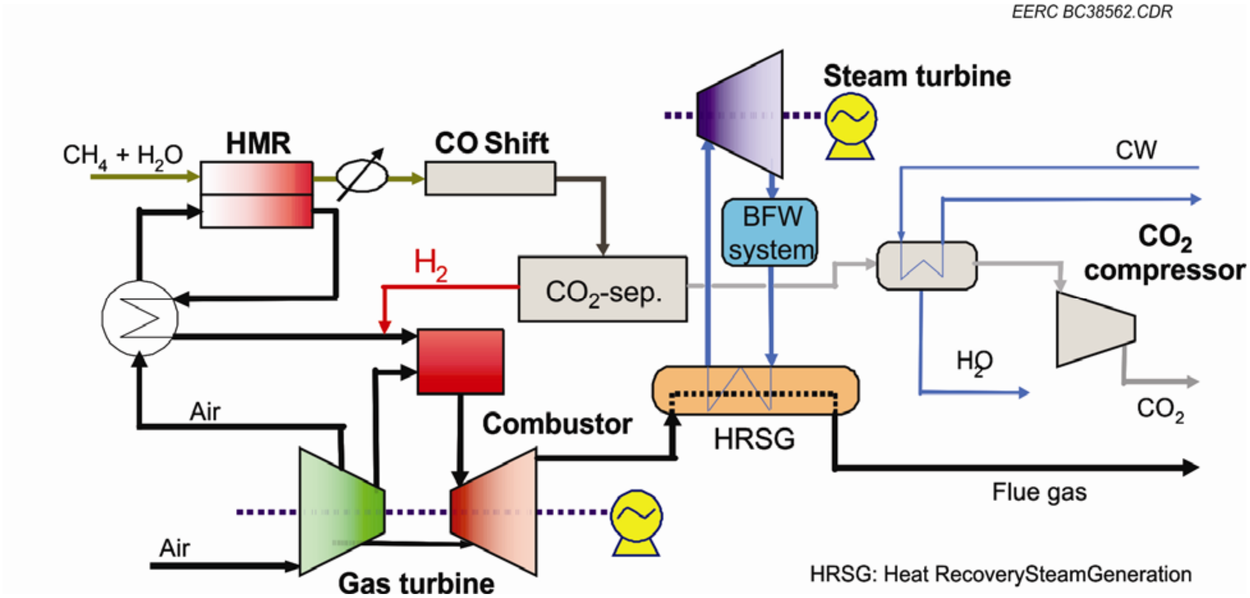


Figure 51. Sketch of the new HMR process with HMR syngas reactor and separate CO_2 removal unit (taken from Smith and others, 2009).

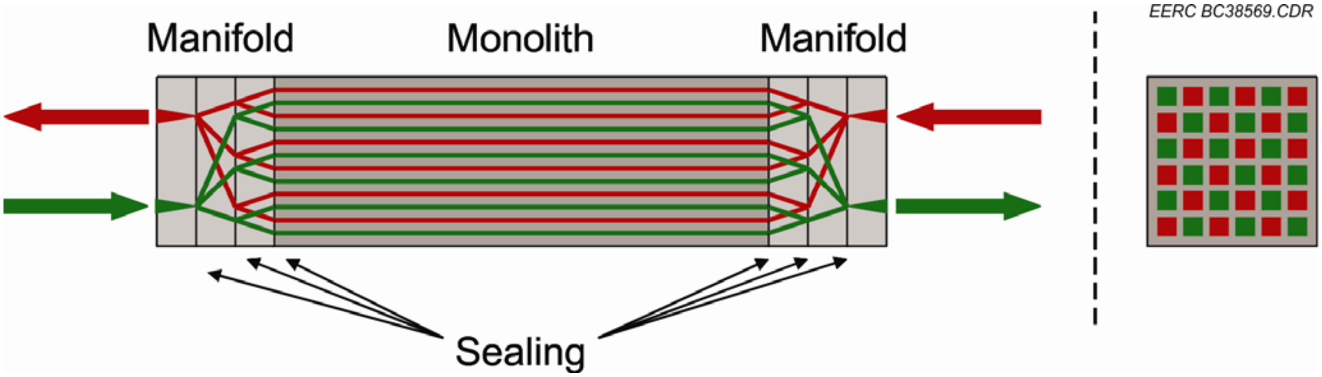


Figure 52. HMR monolith (taken from Smith and others, 2009).

been conceptualized that would have a capacity for reforming 800–900 MW (LHV) natural gas to syngas sufficient for generating 400 MW_e (Smith and others, 2009).

Since start-up in 2001, the development of the HMR gas power cycle has been financed by CCP, with cofunding from the Research Council of Norway. A new, less complicated HMR gas power cycle has been developed and benchmarked. The efficiency loss and CO_2 capture rate are typically 8% and 85%, respectively. These values are lower than what was achievable using the original HMR process. However, because of lower investment costs in the new process, it has a CO_2 avoidance cost that is approximately 20% below the original concept. Small-scale monolith modules have been fabricated and tested under realistic HMR process conditions. Issues found during testing included a low hydrogen flux and difficulty maintaining a high driving force along the reactor (Smith and others, 2009).

Hydrogen Membrane Reactor

A collaborative development partnership operated as part of the European CACHET project has been developing hydrogen membrane reactors for CO_2 capture. The partners include Dalian Institute of Chemical Physics (DICP) from China, SINTEF from Norway, the National Technical University of Athens (NTUA), the Process Design Center (PDC), and Energy Research Centre of the Netherlands (ECN) (Jansen and others, 2010). The membrane is composed of a pure palladium layer deposited on a tubular ceramic support. The manufacture of these by DICP has been scaled up to 50-cm-long, 220-cm^2-membrane-area tubes fitted with high-temperature (700°C), high-pressure (38 bars) end caps provided by ECN. A laboratory-scale process development unit containing eight of the membrane tubes has been constructed and is being tested. This device is capable of producing up to 25 kW_t of H_2 (Jansen and others, 2010).

Inorganic Nanoporous Membranes

The Inorganic Membrane Technology Laboratory at ORNL has developed hydrogen-permeable inorganic membranes for separation of H_2 from syngas streams or the shift gas stream from natural gas reforming, coal gasification, and refinery purge gases. The inorganic membranes, which are three-layer composite membranes that include a nanoporous layer (<5 nm pores) on a microporous layer (~0.5-µm pores) supported on a macroporous support structure (~50-µm pores). Transport through the membranes is by molecular diffusion. It is pressure-driven and is affected by temperature. Separation may occur by surface flow, molecular sieving, Knudsen diffusion, or a combination of these mechanisms. As the temperature is increased, the permeance of hydrogen increases faster than that of CO_2, resulting in larger separation factors (Bischoff and Judkins, 2006). Additional information can be found on the ORNL Inorganic Membrane Technology Laboratory Web site (Oak Ridge National Laboratory, 2010).

High-Temperature Polymeric–Metallic Composite Membranes for H_2/CO_2 Separation

Idaho National Energy and Engineering Laboratory (INEEL) and collaborators with Los Alamos National Laboratory (LANL), Pall Corporation, and Shell Oil Company are developing a polymer membrane for high-temperature membrane CO_2–H_2 gas separations. The membrane is composed of a thermally stable polybenzimidazole (PBI) thin-film composite layer on a porous stainless steel substrate. The resulting composite membrane outperforms other high-temperature membranes in terms of selectivity for the separation of H_2. The metallic support structure allows the membrane to be effective at higher pressures than conventional polymer membranes, and it has been demonstrated at temperatures as high as 400°C. This is a H_2 transport membrane so the CO_2 remains at high pressure, ready for transportation to geological storage (Berchtold and others, 2006).

Additional information on the development of these membranes can be found in the project fact sheet (U.S. Department of Energy National Energy Technology Laboratory, 2008b).

Recently Announced DOE Funding for Membrane Separations for Coal Gasification with Carbon Capture

On July 27, 2010, DOE announced the funding of four projects that will test membrane technology to separate hydrogen and CO_2 from coal or coal/biomass-derived synthesis gas (syngas). Testing will be conducted using actual coal-derived synthesis gas. The projects are intended to advance the technologies toward scale-up to membrane module demonstrations, with the eventual goal of designing and fabricating commercial-scale processes for incorporation into advanced power plants. Technology developers and the technologies receiving funding include the following:

- Praxair, Inc., with partners T3 Scientific and CSM, will demonstrate palladium (Pd) and Pd–alloy membranes on ceramic supports for hydrogen separation from coal-derived syngas.
- United Technologies Research Center will partner with Power+Energy, Inc., to demonstrate hydrogen separation from coal-derived syngas using Pd and Pd–alloy membranes in three forms: dense metal, surface-modified dense metal, and nanocomposite metal membranes.
- Western Research Institute will collaborate with Chart Energy and Chemicals and Synkera Technologies to develop and test planar Pd-based ceramic–anodic aluminum oxide membranes for hydrogen separation from coal-derived syngas streams.
- Worcester Polytechnic Institute will collaborate with Membrane Technology and Research, Siemens Energy America, and T3 Scientific to demonstrate hydrogen separation from coal-derived syngas using Pd and Pd–alloy membranes on porous metal supports.

Further descriptions of the projects are available in the DOE press release about the funding (U.S. Department of Energy, 2010b).

Postcombustion Capture

The September 1, 2010, issue of the *Journal of Membrane Science* is a special issue dedicated to the topic "Membranes and CO_2 Separation." Among the interesting papers in the issue (many of which are cited elsewhere in this document) is a paper by Brunetti and others (2010) that provides the CO_2 permeability and CO_2/N_2 selectivity of many of the "most important" polymer materials, including matrix composite polymer membrane materials. The authors also refer the reader to a paper by Powell and Qiao (2006) that contains a comprehensive review of all polymeric CO_2/N_2 gas separation membranes reported in the literature before the publication of their paper. The interested reader should consult those works if they wish to compare the properties of a newly reported membrane material to those of materials already reported in the literature.

Other key papers in that issue related to postcombustion capture include papers by Zhao and others (2010) and Merkel and others (2010). An important point illustrated in Zhao and others (2010), Merkel and others (2010), and Brunetti and others (2010) is that the optimum membrane properties for purification of CO_2 from flue gas do not call for maximizing both permeance and selectivity but rather to obtain very high permeance for membranes of moderate selectivity. This is illustrated in Figure 53 (the figure was prepared by MTR, makers of the Polaris™ membrane).

MTR Postcombustion CO_2 Membrane

MTR has been funded by NETL to develop and test membrane-based capture of CO_2 from postcombustion flue gas. The work is based on modifications to the membranes and process flows used in their commercial Polaris™ natural gas treatment membrane systems. MTR is also developing CO_2-selective membranes for use in H_2 production applications (Ng and others, 2010).

Figure 54 is the process flow diagram for MTR's system for membrane-based CO_2 removal from flue gas. In this process, countercurrent sweep with combustion air provides a "free" driving force. A CO_2 capture efficiency of 90% can be achieved using about 15% of the plant energy (Merkel and others, 2009). The membrane is a thin-film composite Pebax® membrane made of polyether–polyamide copolymers (U.S. Department of Energy National Energy Technology Laboratory, 2010c). The flat-sheet membranes are packaged into spiral-

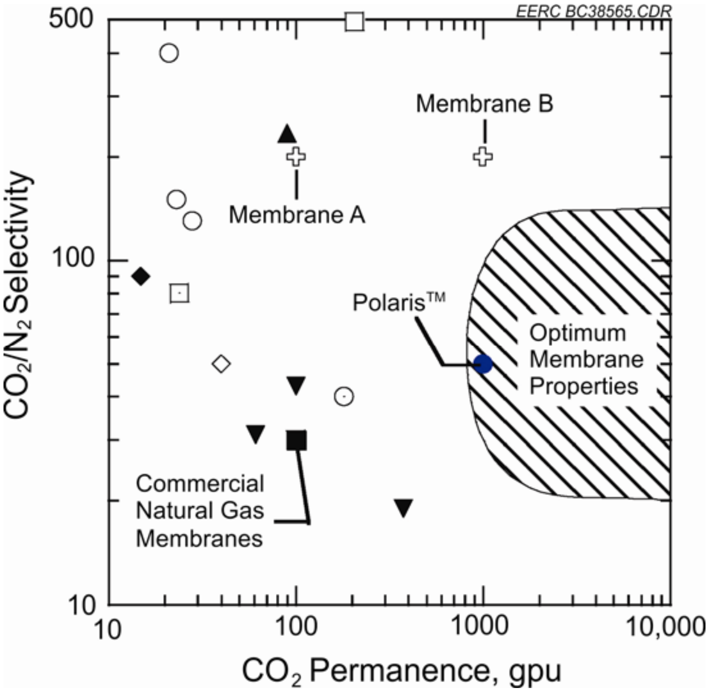


Figure 53. CO_2/N_2 selectivity versus CO_2 permeance plot comparing membrane performance (taken from Merkel and others, 2010).

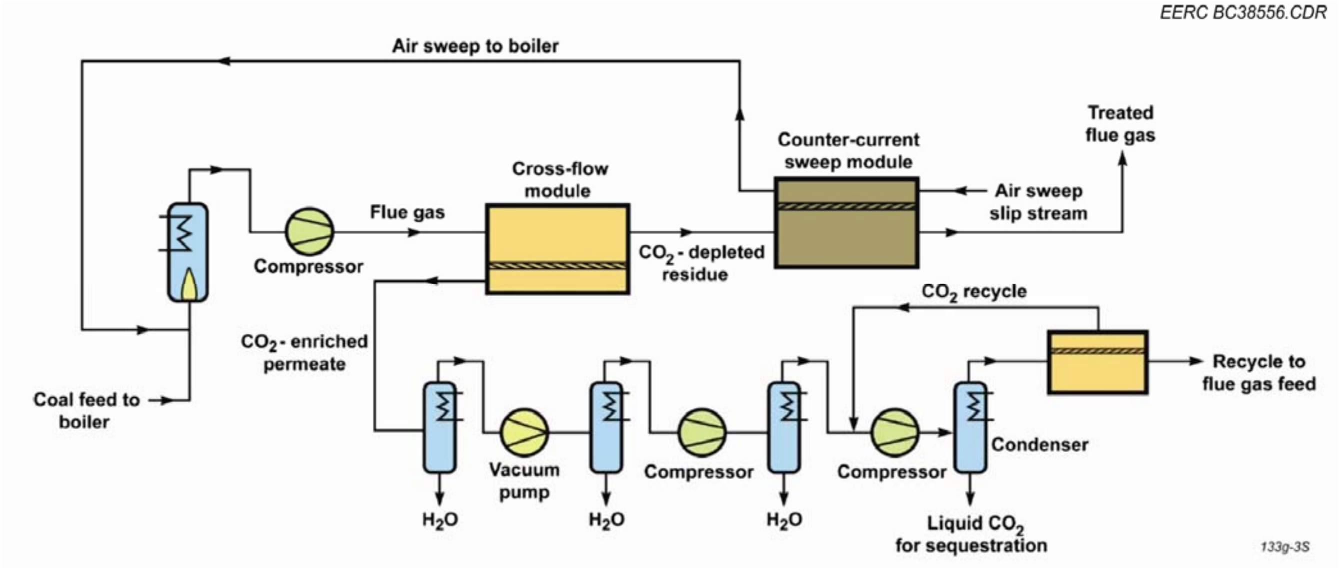


Figure 54. MTR's process design for flue gas CO_2 capture (taken from Merkel and others, 2009).

wound modules. Figure 55 shows MTR's packing design for the membrane modules. These modules have been scaled up to full commercial size. A pilot demonstration project of MTR's system has been initiated at Arizona Public Service's Cholla coal-fired power plant near Phoenix, Arizona. The project was scheduled for start-up in late 2009 at a scale of 250,000 scfd of flue gas, which should capture approximately 1 ton CO_2/day (Merkel and others, 2009). The project will be expanded to a scale of 20 tons CO_2/day (equivalent to the CO_2 generated by 1 MW of power generation) using funds from the DOE and project partners that include MTR, EPRI, Southern Company, and Babcock & Wilcox (Membrane Technology Research, Inc., 2010).

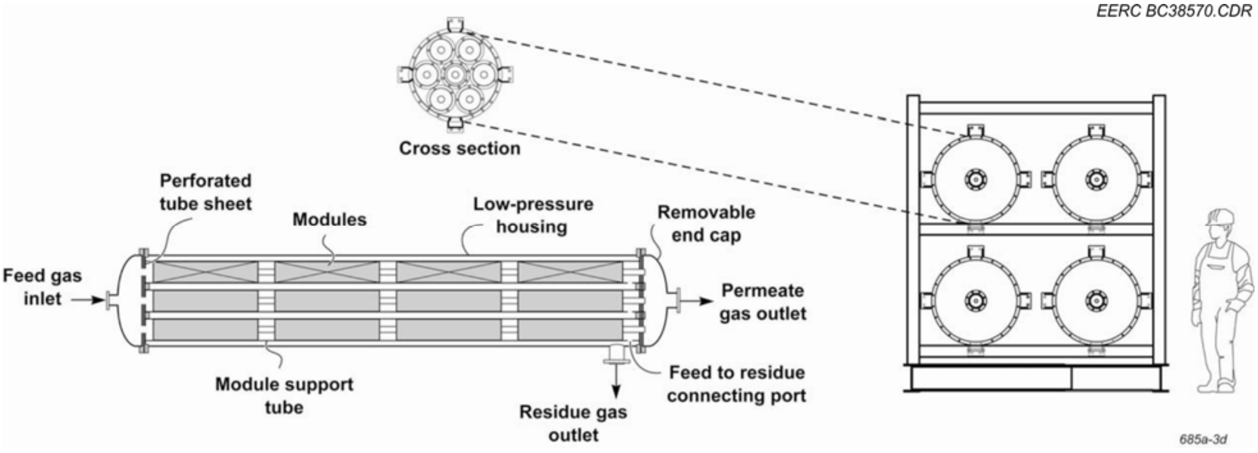


Figure 55. Packing design of the MTR membrane modules (taken from Merkel and others, 2009).

Molecular Gate Membrane

Research Institute of Innovative Technology for the Earth (RITE) has developed composite polymer membranes containing a layer that is highly selective for CO_2. RITE calls these molecular gate membranes (Research Institute of Innovative Technology for Earth, 2010a). The membranes are highly permeable to CO_2 but have low permeability for N_2 and H_2, so they are potentially useful for both postcombustion and precombustion separations. The membrane component that provides for the high selectivity for CO_2 over both N_2 and H_2 is a branched polymer containing multiple amine groups referred to as a modified poly (amidoamine), or PAMAM, dendrimer. Because the PAMAM is actually a viscous liquid, the membrane could be considered a supported liquid membrane. However, since the PAMAM is stabilized in a thin, stable-polymer layer deposited on the surface of a support membrane, its structure and activity are better described as a composite polymer membrane.

RITE has also produced small-scale (1-m-long, 1-in.-diameter) "commercial-sized" modules of PAMAM dendrimer composite membrane. These have been tested at NETL for flue gas separation and were found to be durable for more than 1000 hr of testing using real combustion flue gas (Kazama and others, 2006). RITE is currently focused on improving both the methods of making the membranes and their performance for CO_2/H_2 applications (Research Institute of Innovative Technology for Earth, 2010b).

Gelled Ionic Liquid Membranes

A research group at the University of Colorado at Boulder with considerable experience in developing membrane-based separations and working with ionic liquids received ARPA-E funding to develop novel gelled ionic liquid membranes. The goal is to produce an extremely thin membrane that is highly selective for CO_2 and exhibits a very high CO_2 permeance. The research group recently published a paper on the development of a polymer membrane formed through polymerization of ionic liquid imidazolium compounds, effectively making a true polymer membrane with ionic liquid characteristics (Carlisle and others, 2010).

RTI International –PVDF-Based Polymers

RTI International, with funding from NETL and project partnership that includes Arkema, Arcadis G&M, Generon IGS, and EPA, is developing a postcombustion capture membrane that is made from PVDF (Toy and others, 2009; Toy and Figueroa, 2010). The project includes testing of membrane modules made from Generon's standard polycarbonate hollow fibers, development of new fluorocarbon-based membranes by Arkema, assembly of a test skid for use in 300-hr field testing on coal-fired flue gas, and modeling and economic analysis. The new fluorocarbon-based membranes are expected to be resistant to acids and oxidants, be highly permeable to CO_2, and exhibit long-term durability as well as high thermal stability.

Cryogenic Cooling

Cooling a mixed gas at a pressure of 1 atm to a temperature below the sublimation temperature of CO_2 (i.e., −78.5°C or −109°F) will desublimate CO_2 from the gas phase by forming "dry ice," which is solid CO_2. The gas being treated must be free of water vapor prior to cryogenic cooling. Cryogenic cooling can be applied to previously purified CO_2 and in processing oxycombustion and/or chemical looping flue gas, but the focus here is on cryogenic technologies that may find use in the purification step of carbon capture. Three companies are working in this area: Sustainable Energy Solutions, which is marketing a postcombustion cryogenic CO_2 capture system, and Cool Energy Ltd. and ExxonMobil, which have each developed cryogenic CO_2 capture systems for natural gas that may also prove useful in precombustion capture.

Cryogenic Carbon Capture System

Sustainable Energy Solutions' cryogenic carbon capture (CCC) system is a postcombustion process designed for retrofit applications. The process is said to be cost-effective; to require minimal changes to the existing plant; not to require additional pollution control devices upstream because it is advertised to also remove NO_x, SO_2, HCl, and Hg; to increase turbine efficiency because the turbine outlet steam temperature is lower; and to offer the potential for cooling water savings (Sustainable Energy Solutions, 2010a).

Figure 56 illustrates the CCC process. The flue gas is dried and cooled in a condensing heat exchanger before moderate compression. The compression and cooling steps leave the flue gas at a temperature slightly above the point where CO_2 forms a solid (desublimation occurs at a

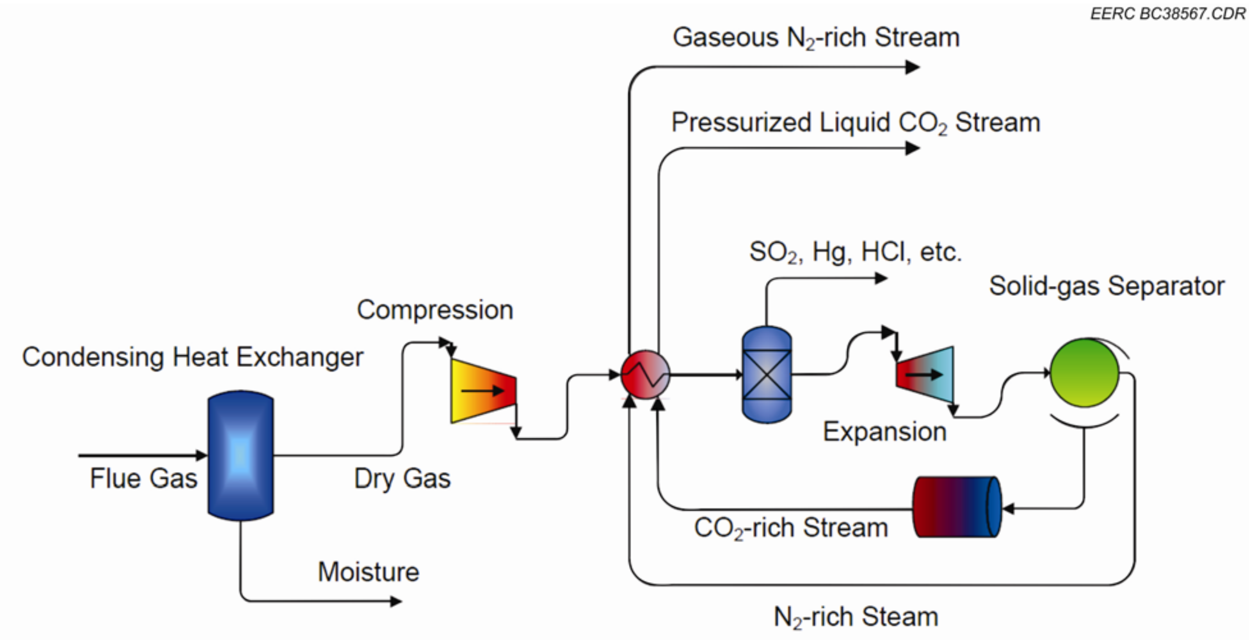


Figure 56. Flow diagram for the CCC process (taken from Sustainable Energy Solutions, 2010b).

temperature of −100° to −135°C, depending on pressure). Solid CO_2 is formed after an expansion step where a decrease in flue gas pressure causes a drop in temperature. The solid CO_2 is separated from the remaining N_2, and both the CO_2 and N_2 are used to cool incoming gases in a recuperative heat exchanger. This step also converts the remaining solid CO_2 back to a liquid at a final pressure of 100–200 atm (Sustainable Energy Solutions, 2010b). An intermediate step that removes NO_x, SO_2, HCl, and Hg is not described.

A paper by Burt and others (2009) provides greater detail on the process and focuses on an economic comparison between the CCC process and oxycombustion. The paper presents estimated levelized costs for electricity and cost per avoided ton of CO_2 for the CCC process based on coal-fired power plant flue gas containing 14% CO_2. The authors show CCC as being between 30% and 45% cheaper than any competing technology, including postcombustion capture with MEA, oxycombustion based on ASU or ITM, as well as IGCC with precombustion capture. The calculated cost was \$33 per ton of avoided CO_2 for CCC versus the average cost of the other four technologies of \$57 per ton of avoided CO_2.

The Clean Coal Technology Fund at the University of Wyoming has provided funding (\$1,405,750) to Sustainable Energy Solutions to "investigate a new design for a fully integrated bench-scale cryogenic carbon capture unit" (University of Wyoming, 2009).

Controlled Freeze Zone (CFZ) Cryogenic CO_2 Separation Process

ExxonMobil developed the CFZ cryogenic CO_2 separation process for capture of CO_2 from natural gas (Gault, 2008). The process is a single-step cryogenic separation that simultaneously removes H_2S and CO_2 from natural gas and produces pipeline-quality natural gas and a liquefied mixed-acid gas that can be used for enhanced oil or natural gas recovery and geologic carbon storage (Northrop and Valencia, 2009). Figure 57 illustrates the process. ExxonMobil has contracted URS to build a commercial-scale CFZ demonstration plant at the ExxonMobil Upstream Research Company Shute Creek Treating Facility near LaBarge, Wyoming (ExxonMobil, 2008). The latest news indicated that construction would be completed and operations initiated in late 2009 (Powerplantccs.com, 2010).

Mineralization

Mineralization is the formation of a carbonate or bicarbonate solid from CO_2. This type of process leaves the carbon in the same oxidation state as the carbon in CO_2, i.e., fully oxidized. The processes described here do not regenerate CO_2 from these solids but, instead, dispose of them or supply them as a product for beneficial reuse. The offerings reviewed in this document are those that combine the capture of CO_2 with the formation of the mineral solid.

To capture CO_2 by mineralization, there must be a source of cations that will form a stable mineral carbonate or bicarbonate (carbonate preferred) as well as sufficient alkalinity to neutralize the acidity of dissolved and hydrated CO_2 (i.e., carbonic acid). The preferred cations are calcium, magnesium, and sodium (both $CaCO_3$ and $MgCO_3$ have very low solubilities; sodium is included because high-sodium-concentration brines [saline water] are widely

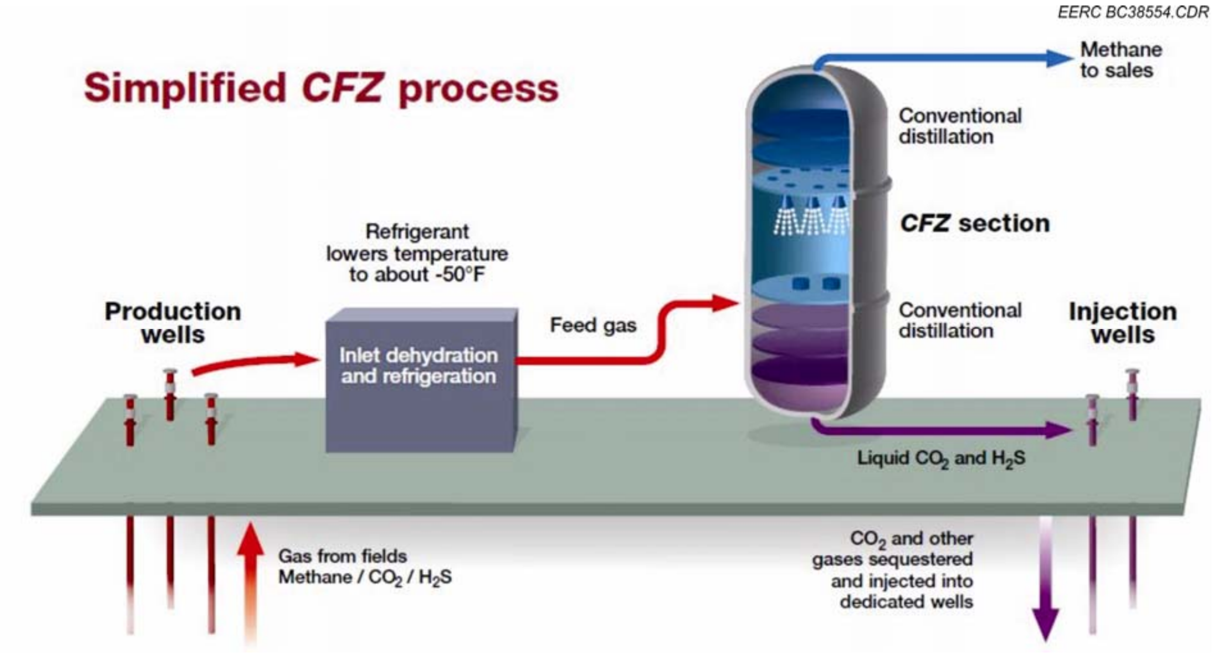


Figure 57. ExxonMobil CFZ technology (taken from Gault, 2008).

available). The cations could be mined, pumped from a well or water body, or found in a waste product. The alkalinity could be mined, found in a waste product, or produced. Processes based on each of these methods have been proposed, tested, studied, and some are even being marketed or readied for market. The key is that, in order to capture the CO_2 permanently as a mineral for disposal or use as a CO_2 mineral-based product, the process must have an input of material and alkalinity (or the production of alkalinity). If the material is readily available and of little or no value or, better yet, is a waste that requires disposal and/or the product is of sufficient value, it may make sense to use the process. In general, it is expected that these processes will find use in niche markets. Entities that are marketing or conducting research in the area of mineralization-based CO_2 capture include Alcoa, the University of Wyoming, Columbia University, Calera, Skyonic, and New Sky Energy.

Alcoa – CO_2 Capture Process with Bauxite Waste

Alcoa developed a CO_2 capture and bauxite waste disposal process that involves mineralization and disposal of CO_2 as a carbonate solid. The process, which is shown in Figure 58, was developed at Alcoa’s Kwinana, Australia, facility (Alcoa, 2007). The bauxite waste is a high-magnesium-content alkaline waste. The waste is contacted with flue gas in an aqueous suspension, and the CO_2 reacts with the hydroxide alkalinity to form bicarbonate ions and then carbonate ions. The carbonate ions precipitate out as magnesium carbonate solids. The neutralized waste is dried and disposed of in a landfill, as fill at the bauxite mine, or beneficially used as road base, building materials, or as a soil amendment.

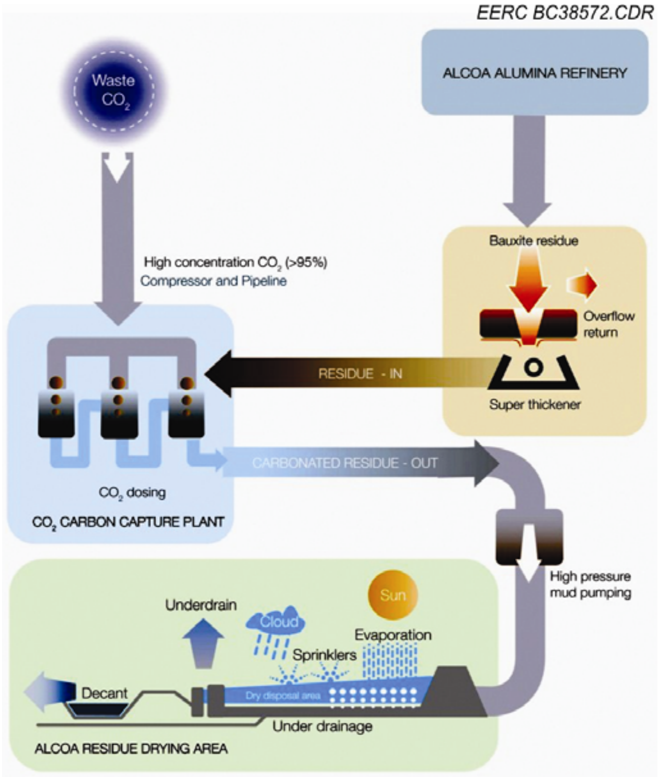


Figure 58. Alcoa CO_2 capture system (taken from Alcoa, 2007).

In a cooperative research project between NETL and Alcoa, a mixture of bauxite residue and saline water was tested for its ability to capture CO_2 (Dilmore and others, 2008). A 90:10 (by volume) bauxite residue-to-brine mixture exhibited a CO_2 sequestration capacity of greater than 9.5 g/L when exposed to pure CO_2 at 20°C and 0.689 MPa. The laboratory test also suggested that the CO_2 sequestration capacity of the samples increases with aging.

Alcoa has continued to improve the process and was recently selected to receive Phase II funding from DOE for a demonstration project (U.S. Department of Energy National Energy Technology Laboratory, 2010g). From the information provided in the press release, it appears that the exact process being used has changed from that shown in Figure 58 although the source of alkalinity and the metal cations used for mineral formation remain the same.

Alkaline Fly Ash-Based CO_2 Capture

Reddy and others (2010) studied the use of alkaline coal combustion fly ash to capture flue gas CO_2. The flue gas CO_2 concentration was observed to decrease from 13.6% to 9.6%, and the total carbon (as $CaCO_3$) content of the fly ash increased from <0.02% to 3.9%. Hg and SO_2 removal and mineralization were also observed. A preliminary economic analysis of the process for 90% CO_2 capture from a 532-MW power plant yielded a mineralization cost of \$11/tonne CO_2 at a mineralization capacity of 207 kg CO_2/tonne fly ash.

Additional information on the project is available on the University of Wyoming Research Products Center Web site (University of Wyoming, 2010).

Accelerated Weathering

The idea of using accelerated weathering of rocks containing high magnesium and calcium concentrations was first popularized in the 1990s by Dr. Klaus Lackner when he was at LANL (Lackner and others, 1995, 1998). In that work, he and his colleagues identified basaltic ultramafic rocks as a good source, but difficulties with accelerated weathering stalled the progress toward commercialization.

One of Dr. Lackner's colleagues at Columbia University, Dr. Ah-Hyung Park, has worked on the problem of accelerated weathering (Park and others, 2003). The weathered mineral produces the calcium and magnesium as metal hydroxide, eliminating the need for added alkalinity. The work focused on the use of chelating agents to accelerate weathering. Lackner and Park also have funding from New York State Energy Research and Development Authority to investigate the use of wollastonite deposits in New York state for the process (Lackner and Park, 2010). The conceptual process can lead to minerals for disposal or beneficial use as illustrated in Figure 59.

Calera

Additional work being done on CO_2 capture through mineralization includes the work by Calera Corporation. In their process, shown in Figures 60 and 61, the CO_2 is combined with minerals harvested from waste products including fly ash and/or brines (potentially waste brine from seawater desalination) and alkalinity produced electrochemically (using the brines)

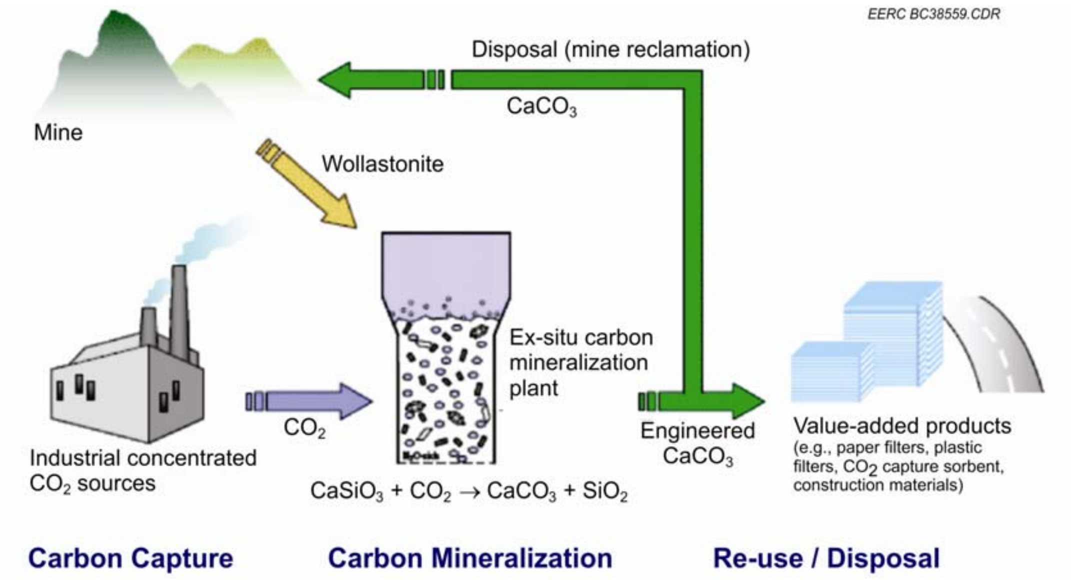


Figure 59. Accelerated weathering of high-magnesium-content minerals (taken from Lackner and Park, 2010).

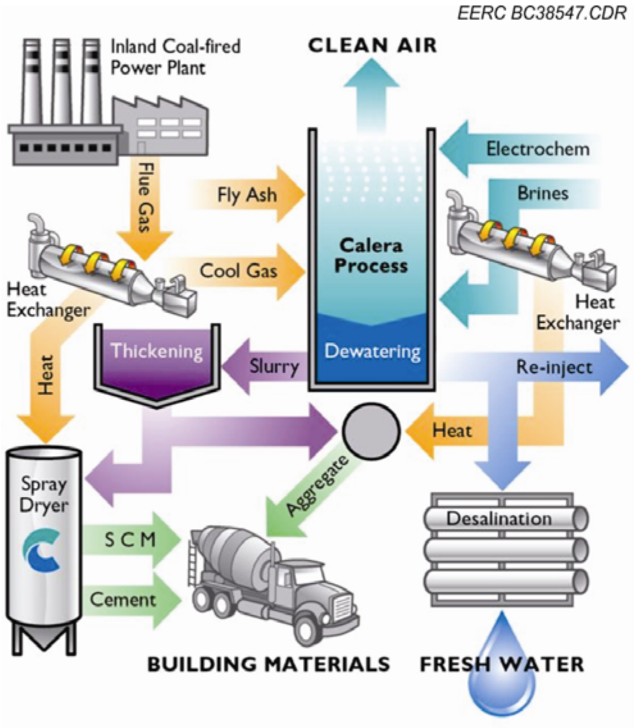


Figure 60. Calera CO_2 capture and mineralization process (taken from Calera Corporation, 2010b).

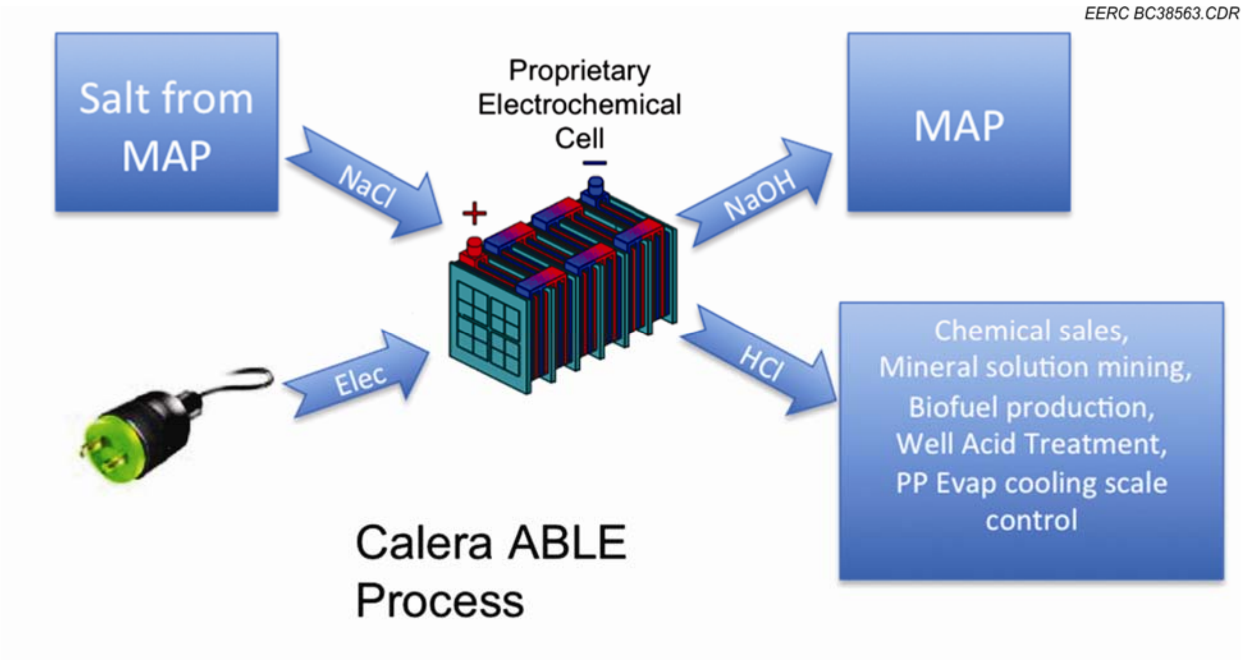


Figure 61. Electrochemical generation of alkalinity for the Calera CO_2 capture and mineralization process (taken from Calera Corporation, 2010a).

(Calera Corporation, 2009). As shown in Figure 61, if the brine is sodium chloride (NaCl), the electrochemical process produces NaOH and HCl. The NaOH could be used in the Calera process, presumably to produce Na_2CO_3 as the product of CO_2 capture. The gas–liquid contacting system employed by the process is the NeuStream contactor from Neumann Systems Group (Calera Corporation, 2009). The HCl would be sold as a product.

DOE and the Australian government are currently funding a project based on this process. The project at Moss Landing, California, is located at a site formerly used for extracting magnesium from seawater. Calera has been operating a CO_2 pilot plant at the site of the Moss Landing Cement Company for the last few years using flue gas from Dynegy's Moss Landing gas-fired power plant as the CO_2 source. They have also operated a 0.3-MWth-equivalent coal-fired boiler simulator (AllBusiness, 2010). In September 2009, DOE awarded a grant for expansion of the Moss Landing facility to demonstration scale, treating a 50-MW-equivalent slipstream from the Dynegy plant (AllBusiness, 2010).

Calera has been funded to perform a demonstration of its process on flue gas from the lignite-fired Yallourn plant in Australia's Latrobe Valley) (AllBusiness, 2010). This demonstration will be at least 10-MW-equivalent in size.

C-Quest Chemical Sorbent System

The C-Quest chemical sorbent system is designed to significantly reduce CO_2 emissions from utility and industrial boilers. The sorbent ingredients are widely available, and the by-product is a recyclable solid that can be disposed of safely. Capture rates are dependent on several factors, including gas-to-sorbent ratios, temperatures, and retention times, although CO_2 capture rates as high as 90% were obtained during laboratory testing at the EERC. The sorbent captures other pollutants as well. In the laboratory, capture rates as high as 99% SO_2, 90% mercury, and 15% NO_x were observed concurrently with the CO_2 capture. Further testing is being performed to determine capture efficiencies and other information required to determine an ultimate cost per ton of CO_2 captured. Current results are promising (Pavlish and others, 2008).

SkyMine® Process

Skyonic Corporation has developed the SkyMine process, a technology that uses brine as a source of mineral ions for precipitation of solid carbonates and bicarbonates. Electrolysis is used to produce hydroxide alkalinity for the formation of the carbonates and bicarbonates upon absorption of CO_2. The CO_2 ends up as solid $NaHCO_3$. Skyonic also claims that the process removes SO_x, NO_2, and mercury (Skyonic, 2010). Skyonic has reported that it is conducting its first commercial-scale pilot project at the Capitol Aggregates, Ltd., cement plant in San Antonio, Texas (Yahoo Finance, 2010). Construction of this facility began in April 2010 (San Antonio Business Journal, 2010).

New Sky Energy

New Sky Energy (NSE) is a Colorado-based company that is also working on a CO_2 mineralization process based on electrochemical processing of brine and conversion of CO_2 to

Na_2CO_3. NSE claims that the process can trap 1.1 tons of CO_2 per ton of NaOH and that it produces materials that can be used in the manufacture of plastics, glass, and other goods (Jaffe, 2010). According to an NSE patent application (Little and others, 2008), the system is designed to produce hydrogen, oxygen, base, and acid using electrochemical processes fed with power that can be derived from a renewable energy source (most likely solar and/or wind power). The company also has submitted a patent application that reveals a direct solar-to-water hydrolysis process that would eliminate the need for photovoltaic solar- or wind-generated electricity.

In January 2010, NSE and CSM announced that NSE would fund a project at CSM to build a fully operating, scalable model of the New Sky electrochemical carbon capture technology (Colorado School of Mines, 2010).

Cemtrex – Carbondox Process

Cemtrex is developing a mineralization-based CO_2 capture process called the Carbondox process. The process captures CO_2 from coal-fired flue gas using a corona catalyst and operates via bicarbonate mechanisms in an aqueous medium. The process would be installed after the FGD equipment at a pc power plant (Cemtrex, 2010).

Reduction

Reduction is the chemical transformation of the oxidized carbon to a reduced state through the input of energy during the application of chemical, photochemical, electrochemical, and/or biological processes. This concept incorporates the CO_2 into an organic compound such as a polycarbonate plastic, a fuel, or some other desired product. All of these processes require energy to form at least one carbon–carbon or carbon–hydrogen bond. When a fuel made from reduced CO_2 is used to provide the energy for the reduction process, more energy is required to make the fuel or other product than is present in the product. Therefore, the process makes sense from an energy balance perspective only when the reduced carbon product is of high value, the fuel is effectively an energy storage product made from an intermittent energy supply source (e.g., wind, solar), and/or the fuel produced is useful in ways that the original source fuel was not (e.g., production of a transportation fuel from coal-derived CO_2).

Photosynthesis

Closed-Environment Agriculture

It is not uncommon for large greenhouse operations to use bottled CO_2 or CO_2 produced from the combustion of propane or natural gas to supplement the CO_2 available in ambient air during intensive greenhouse production of food crops and flowers (Blom and others 2002). WarmCO_2, a company in Terneuzen, the Netherlands, provides industrial waste heat, anhydrous ammonia, and CO_2 from a fertilizer production facility to a 250-ha greenhouse horticultural complex (Warm CO_2, 2010; Rijckaert, 2009). Other flue gas CO_2-to-closed environment agriculture examples likely exist, but a thorough review of this area was beyond the scope of this report.

Algae and Microalgae

Capture of CO_2 from combustion flue gas for direct use in algae production has been widely investigated and has been applied commercially. The processes that show the most promise are open-raceway algal ponds. Several projects attempted with photobioreactors have failed based on economic analysis because of the cost of the reactor systems (Benneman, 2008a,b). For open raceways, the two choices for capture are direct sparging of the flue gas through the water in the algal growth pond or raceway and use of an absorption tower. The former requires a huge distribution system for the flue gas and would be expected to provide low capture rates. The second requires transport of the growth medium and growth of the algae in relatively high-alkalinity waters in order to ensure sufficient absorption capacity.

DOE funded an algae biofuels program through the National Renewable Energy Laboratory from 1978 through 1996. The closeout report contains the lessons learned during that program, including issues related to growth of algae using CO_2 captured from flue gas (Sheehan and others, 1998).

Other companies that are evaluating the capture of CO_2 using algae are discussed in the following text. It should be noted that this is a limited review of the many (mostly small start-up) companies that hope to capitalize on interest in the use of algae for CO_2 capture and the production of biofuel, omega-3-rich oils, or other products.

Cyanotech Corporation

Cyanotech Corporation operates a 2-MW_e combined-heat-and-power fuel oil/diesel generator system with a flue gas scrubber for CO_2 capture. The growth medium used for growing a type of algae called spirulina is contacted with 8% CO_2 flue gas (equaling 188 kg/hr CO_2) in an absorption tower. The company reports a CO_2 capture efficiency of 75% and a capture rate of 67 tons/month of CO_2. This is used to grow approximately 36 tons/month of spirulina in an estimated 12 ha of algal ponds (Pedroni and others, 2001). The spirulina is marketed as a food and a nutritional supplement (Cyanotech, 2010).

Seambiotic

Seambiotic has been developing a process for cultivating algae using flue gas from coal-fired power stations. The algae captures the CO_2 from the flue gas and will be used to produce omega-3 fatty acid and biofuels products (Seambiotic, 2010). The company currently operates a 1000-m^2 pilot-scale system at a power plant in Ashkelon, Israel (EcoSeed, 2010), and is in the process of scaling up to large-scale industrial algae cultivation and production.

Pond Biofuels

Pond Biofuels has built an algae production facility using raw cement production emissions as algae feedstock. The system is said to be a cost-effective method for scrubbing CO_2 (Pond Biofuels, 2010). It is planned that the algae will be dried using waste heat from the cement plant and burned as fuel in the cement kilns. Alternatively, the algae could be processed into fuel for the cement company's fleet of trucks (Hamilton, 2010).

Other Biofuels-from-Algae Projects

On July 22, 2010, DOE announced funding for two flue gas CO_2-to-algal-based-biofuel production projects (U.S. Department of Energy National Energy Technology Laboratory, 2010g); the project descriptions are summarized in the following text.

Touchstone Research Laboratory

Touchstone Research Laboratory Ltd. will pilot-test an open-pond algae production technology that is capable of capturing a minimum of 60% of the CO_2 contained in the flue gas from an industrial coal-fired source. The project objective is the production of biofuel and other high-value coproducts. A novel phase change material will cover the algae pond surface to regulate temperature, reduce evaporation, and control the infiltration of invasive species. Oils extracted from harvested algae will be converted to biofuel. An anaerobic digestion process will tested for the conversion of residual biomass to methane.

Phycal

Phycal will complete development of an integrated system designed for the production of liquid biocrude from algae that has been cultivated using captured CO_2. It is possible to blend the algal biocrude with other fuels for power generation or to process it into a variety of renewable replacement fuels such as jet fuel and biodiesel. Phycal will design, build, and operate the facility in Hawaii.

Funded by Vattenfall

On July 23, 2010, the Swedish utility Vattenfall announced that it had launched a pilot project to grow algae in a greenhouse environment. Vattenfall plans to investigate the economics of using the technology to reduce CO_2 emissions from coal-fired power plants (Vattenfall, 2010). The algae will be used to produce biodiesel, biogas, and nutrient supplements for aquaculture (fish farming).

Chemical and Biochemical Processes

Considerable effort is being made to find ways to economically use CO_2 to make useful products without requiring photosynthetic organisms or forming minerals. These efforts are sometimes combined with the CO_2 capture process rather than just using the captured CO_2 as a resource. This section of the report is not a comprehensive listing or analysis of all of the processes under investigation but rather provides information concerning the breadth of these efforts and direction to where the reader might find additional information.

Production of Polymers

Numerous research groups have investigated the use of CO_2 as a resource for the manufacture of plastics and other chemical products. In fact, it is common for CO_2 to serve as resource in the manufacture of polycarbonate plastics. The first reports of CO_2 incorporation into polycarbonates using epoxides were published in the 1960s. The focus of the work listed here is the direct use of CO_2 in flue gas as the CO_2 resource for polymer synthesis.

Polycarbonates are not the only chemical synthesis product that can be made from CO_2. The interested reader is referred to a recent article by Riduan and Zhang (2010) that reviews chemical product synthesis using CO_2 under “mild conditions.” In the article, the authors avoid spending time on the “coupling of epoxides with CO_2 to form cyclic carbonates or polycarbonates because they have been well documented.” Instead, they refer to the reader to several recent works and review articles on that topic.

One of the projects funded as part of DOE’s American Reinvestment and Recovery Act – Industrial Sources into Useful Products Program is a CO_2-to-polycarbonate plastics project (U.S. Department of Energy National Energy Technology Laboratory, 2010g). Novomer Inc. will team with Albemarle Corporation and the Eastman Kodak Co. to develop a process to convert waste CO_2 into a number of plastics for use in the packaging industry. Novomer has a novel catalyst technology that reacts CO_2 with petrochemical epoxides, creating a family of thermoplastic polymers that are composed of up to 50 wt% CO_2.

Generation of “ElectroFuels”

Through the ARPA-E program, DOE has provided funding for several “ElectroFuels” projects designed to find ways to convert CO_2 to liquid fuels. For the most part, these projects do not employ organisms that normally perform photosynthesis or add the use of electricity to help drive their metabolism. Rather, the ARPA-E objective is for projects to employ “metabolic engineering and synthetic biological approaches for the efficient conversion of carbon dioxide to liquid transportation fuels.” The projects which have been funded include the following:

- Columbia University – Biofuels from CO_2 Using Ammonia-Oxidizing Bacteria in a Reverse Microbial Fuel Cell
- Ginkgo BioWorks – Engineering *E. Coli* as an Electrofuels Chassis for Isooctane Production
- Harvard Medical School–Wyss Institute – Engineering a Bacterial Reverse Fuel Cell
- Lawrence Berkeley National Laboratory – Development of an Integrated Microbial-ElectroCatalytic System for Liquid Biofuel Production from CO_2
- Massachusetts Institute of Technology – Bioprocess and Microbe Engineering for Total Carbon Utilization in Biofuel Production

- Massachusetts Institute of Technology – Engineering Ralstonia eutropha for Production of Isobutanol Motor Fuel from CO_2, H, O_2

- Medical University of South Carolina – Electroalcoholgenesis–Bioelectrochemical Reduction of CO_2 to Butanol

- North Carolina State University – Hydrogen-Dependent Conversion of Carbon Dioxide-to Liquid Electrofuels by Extremely Thermophilic Archaea

- OPX Biotechnologies, Inc. – Novel Biological Conversion of Hydrogen and Carbon Dioxide Directly into Biodiesel

- Pennsylvania State University – Development of Rhodobacter as a Versatile Platform for Fuels Production

- Regents of the University of California, Los Angeles – Electro-Autotrophic Synthesis of Higher Alcohols

- The Ohio State University – Bioconversion of Carbon Dioxide to Biofuels by Facultatively Autotrophic Hydrogen Bacteria

- University of Massachusetts Amherst – Electrofuels via Direct Electron Transfer from Electrodes to Microbes

Descriptions of these projects can be found through the ARPA-E Web site (U.S. Department of Energy Advanced Research Projects Agency – Energy, 2010d).

STEP Carbon Capture

Recently, researchers at George Washington University and Howard University in Washington, D.C., published a paper on a closely related topic (Licht, and others, 2010). In their paper, they describe experimental results from their development of a process they call STEP (Solar Thermal Electrochemical Photo) carbon capture. The authors conclude that CO_2 can be captured at a solar energy efficiency from 34% to over 50% and that the process can be used to produce solid carbon or CO and H_2 that can be used to synthesize solar diesel fuel, synthetic jet fuel, or other chemicals.

EVALUATION AND DIRECT COMPARISON OF CAPTURE TECHNOLOGIES BY THE PCO_2C

The PCO_2C at the EERC is a multiclient-funded program separate from the PCOR Partnership that is focused on CO_2 capture technology testing, demonstration, and development. It is funded in part by DOE and in part by industry and utility participants. PCO_2C is a multiple-phase program. Phase I was recently completed, and Phase II was initiated. Phase I included the addition of oxycombustion and postcombustion testing capabilities to an existing fuel-flexible combustion test unit (coal, natural gas, biomass) that operates at approximately 550,000 Btu/hr (about 60 to 100 coal feed lb/hr). This system already included an SCR unit, an ESP, a fabric filter, wet FGD, and a spray dryer absorber as well as facilities for testing ash fouling, flame behavior, and other aspects of concern with respect to coal combustion. Retrofit for oxycombustion using pure O_2 and recycled flue gas allowed for operation at conditions that yielded flue gas CO_2 concentrations as high as 85% and over 90% for short periods of time. The retrofit for postcombustion capture included the addition of a solvent absorber–stripper system for CO_2 capture. Three solvents were tested in Phase I: MEA as a base case, a mixture of MDEA and PZ, and a proprietary solvent, H3-1 from Hitachi. Engineering and economic analysis performed based on the experimental results from the oxycombustion and postcombustion tests revealed that the least-cost alternative in terms of both energy penalty and cost of electricity (COE) was the use of H3-1. Phase II work will include testing of additional solvents and the Neumann systems contactor (Neustream-C) as an alternative to the traditional column-based absorber–stripper as well as the addition of solid sorbent testing.

SUMMARY

Considerable effort is being expended to develop a variety of cost-effective CO_2 capture technologies capable of meeting the DOE goals of 90% capture of CO_2, 95% pure CO_2 product, and an increase in COE no greater than 35%. Some commercially available technologies can meet the first two of these three goals, but even these have not yet been demonstrated for use at full utility scale for coal-derived power generation. These commercial technologies, which have estimated COE increases that are higher than the target, likely will be demonstrated at utility scale in the next 3 to 5 years.

Emerging processes that have completed smaller-scale pilot tests and are in the process of scaling up to larger demonstrations are likely to be available commercially in the next 5 to 10 years. Some of these technologies may meet the DOE goal.

Many other technologies still require extensive development, testing, and demonstration before it will be known if they can reach DOE's goals. The technologies that are the most similar to existing technologies (e.g., new aqueous solution-based absorption solvents) will take much less time to enter the market than those technologies for which there is little industrial or commercial experience or which require significant development and scale. A few of these early-stage technologies offer the hope of being "game changers"—technologies that dramatically reduce CO_2 emissions at very low cost–although it is difficult to know how much promise they will fulfill while they are still early in the development cycle.

Despite the existing effort, there is still room for all entities with an interest or expertise in the area of CO_2 capture to be involved in addressing this critical research need by offering new concepts, improving on existing concepts, and providing advice, guidance, and crucial funding toward further research, development, demonstration, and commercialization of CO_2 capture technologies.

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APPENDIX A

CO_2 CAPTURE TECHNOLOGIES

CO_2 CAPTURE TECHNOLOGIES

This information is provided as a way to quickly compare the technologies described in the body of the report. For each technology, the reader is provided with the technology name, the developer, the status of development (laboratory research, small- or large-scale demonstration, commercially available), and basic information on the process.

The information is organized into three sections, one for each capture platform: precombustion, during combustion, and post combustion. ***It is important to note that this organization scheme differs from that of the body of the report*** and was done to aid the reader in comparing technologies within the platform(s) of interest to them. Some technologies are applicable to more than one capture platform and, therefore, are listed in the table more than once. In general, the information provides relatively little technical detail and no references to literature. The reader is urged to consult the body of the report to find greater detail on a given technology, citations to literature resources, and for background information concerning the general technical approaches used for CO_2 capture.

PROCESS	DEVELOPER(s)/ SUPPLIER(S)	CLASSIFICATION	STATUS	CHEMICAL(S)	NOTES
PRECOMBUSTION High partial pressures of CO_2 are more favorable for use of physical solvent absorption and pressure swing adsorption using physical adsorbents.					
Physical Solvent-Based Absorption Processes					
Selexol™	UOP LLC	Physical solvent absorption	Commercial for gas processing	Mixture of dimethyl ethers of polyethylene glycol	Double-stage Selexol process removes both H_2S and CO_2 from high-pressure gas streams. It is capable of providing purified CO_2.
Rectisol®	Linde/Lurgi	Physical solvent absorption	Commercial for gas processing; in active use at the Great Plains Synfuels Plant	Methanol	Very low temperatures are needed. This is used for CO_2 capture from syngas at the Great Plains Synfuels Plant. The purified CO_2 is then compressed and shipped by pipeline to Canada for enhanced oil recovery.

PROCESS	DEVELOPER(s)/ SUPPLIER(S)	CLASSIFICATION	STATUS	CHEMICAL(S)	NOTES
Purisol®	Lurgi	Physical solvent absorption	Commercial for gas processing	N-methyl-2-pyrrolidone	Purisol process is virtually identical to Rectisol. Applied to the gas produced from partial oxidation of heavy oils or coal gasification, primarily for sulfur recovery.
JEFFSOL®–PC (Fluor solvent process)	Huntsman Chemicals	Physical solvent absorption	Commercial for gas processing	Propylene carbonate	Application is low-H_2S syngas.
Morphysorb	Uhde GmbH	Physical solvent absorption	Commercial for gas processing	N-formyl-morpholine (NFM) and N-acetyl-morpholine (NAM)	Similar to the Selexol process.
Ionic Liquids	Various	Physical solvent absorption	Research – laboratory scale	Physical solvent ionic liquids	
Mixture of Chemical and Physical Solvents					
Sulfinol®	Shell	Absorption process using a mixture of a physical solvent and a chemical solvent	Commercial for gas processing	Sulfolane – physical solvent; DIPA (diisopropanolamine) chemical solvent	Typically used for gas with a H_2S-to-CO_2 ratio greater than 1:1 or where it is not necessary to remove the CO_2 to the same levels as is required for H_2S removal.

PROCESS	DEVELOPER(s)/ SUPPLIER(S)	CLASSIFICATION	STATUS	CHEMICAL(S)	NOTES
Chemical Solvent-Based Absorption Processes					
Hot Potassium Carbonate-Based Processes Inorganic and organic catalysts are commonly used with metal carbonate processes, because without them, slow reaction kinetics limit performance. Pressure of feed gas is 150 to 300 psi so not typically applicable to postcombustion.					
CATACARB®	Eickmeyer & Associates	Chemical solvent absorption	Commercial for gas processing (ammonia plants, natural gas, ethylene oxide)	Hot potassium carbonate with catalyst	Applicable for CO_2 partial pressures above a minimum of 210 to 345 kPa (30.5 to 50 psi) with an optimum of 700 kPa (101.5 psi).
Benfield™	UOP LLC	Chemical solvent absorption	Commercial for gas processing (ammonia plants, natural gas, ethylene oxide)	Hot potassium carbonate with catalyst	Applicable for CO_2 partial pressures above a minimum of 210 to 345 kPa (30.5 to 50 psi) with an optimum of 700 kPa (101.5 psi).
Flexsorb® HP	Exxon	Chemical solvent absorption	Commercial for gas processing (ammonia plants, natural gas, ethylene oxide)	Hot potassium carbonate with hindered amine activator	

PROCESS	DEVELOPER(s)/ SUPPLIER(S)	CLASSIFICATION	STATUS	CHEMICAL(S)	NOTES
Other	Giammarco-Vetrocoke	Chemical solvent absorption	Commercial for gas processing (ammonia plants, natural gas, ethylene oxide)	Hot potassium carbonate with organic activator	
Amine-Based Processes Chemical solvents (typically amines) can be used for precombustion separations but they tend to be preferable to the physical solvents only under lower-CO_2–partial-pressure conditions.					
MEA	Various	Chemical solvent absorption	Commercial for gas processing	Monoethanolamine (MEA) (primary amine)	MEA is used for removal of H_2S and CO_2 from natural gas and syngas, but it is not anticipated to be an important solvent for use in precombustion CCS applications. It is probably the most popular chemical solvent used for H_2S removal.

PROCESS	**DEVELOPER(s)/ SUPPLIER(S)**	**CLASSIFICATION**	**STATUS**	**CHEMICAL(S)**	**NOTES**
MDEA	Various	Chemical solvent absorption	Commercial for gas processing	Methyldiethanolamine (MDEA) (secondary amine)	MDEA is probably the most popular amine used in gas processing for CO_2 removal. Often a catalyst is added to increase the rate of CO_2 absorption.
aMDEA®	BASF	Chemical solvent absorption with catalyst	Commercial for gas processing	Methyldiethanolamine (MDEA) (secondary amine) with catalyst (activator)	Registered process employing activated MDEA.
Physical Adsorption					
Pressure-Swing Adsorption Pressure swing adsorption is commonly used for oxygen purification but is typically more expensive at large scale than cryogenic distillation. Pressure swing adsorption can also be used for CO_2 removal from syngas and natural gas.					
Zeolite	Various	Physical adsorption	Commercial for gas processing		
Activated Carbon	Various	Physical adsorption	Research – laboratory scale		
Carbon Nanotubes	Various	Physical adsorption	Research – laboratory scale		

PROCESS	DEVELOPER(s)/ SUPPLIER(S)	CLASSIFICATION	STATUS	CHEMICAL(S)	NOTES
Carbon-Based Sorbent	Advanced Technology Materials and SRI International	Physical adsorption	Research – laboratory scale		The groups are working together on a novel carbon-based sorbent for CO_2 adsorption.
Electrical Swing Adsorption	Oak Ridge National Laboratory; University of Porto, Portugal; Centre National de la Recherche Scientifique, Nancy, France; University of Queensland, Australia	Physical adsorption	Research – laboratory scale		Carbon fiber composite molecular sieves most commonly serve as the solid sorbent and/or solid sorbent support. A low-voltage current is used to remove the adsorbed CO_2 by resistive heating of the sorbent.

PROCESS	DEVELOPER(s)/ SUPPLIER(S)	CLASSIFICATION	STATUS	CHEMICAL(S)	NOTES
Chemical Adsorption					
Chemical-Looping Combustion	ALSTOM, Korean Institute of Energy Research, Vienna University of Technology, Chalmers University	Chemical adsorption	Research to small pilot scale. Largest system run to date is 65-kW$_{th}$ with a 3-MW$_{th}$ system planned.	Metal oxides used as oxygen adsorbents	Process uses O_2 provided by metal oxide carriers to combust the fuel, producing CO_2 and water. Condensation of the steam produces a relatively pure stream of CO_2.
Magnesium Hydroxide-Containing Sorbents	National Energy Technology Laboratory	Chemical adsorption	Research – modeling	Magnesium hydroxide (MgOH)	Investigating the use of magnesium hydroxide-containing sorbents for precombustion CO_2 capture. These sorbents show good potential for use at high pressure and high temperature.

PROCESS	DEVELOPER(s)/ SUPPLIER(S)	CLASSIFICATION	STATUS	CHEMICAL(S)	NOTES
Magnesium Oxide	Illinois Institute of Technology and the Gas Technology Institute	Chemical adsorption	Research – laboratory scale	Magnesium oxide (MgO)	The magnesium oxide regenerable adsorption process removes CO_2 from raw syngas at the temperatures and pressures typically encountered in gasification.
Calcium Oxide-Based Adsorbents	Pacific Northwest National Laboratory	Chemical adsorption	Research – laboratory scale	Calcium-oxide-based materials (CaO)	This work has been performed with calcium oxide-based adsorbents at elevated temperatures.
Sorption-Enhanced Water–Gas Shift Reaction	Air Products and Chemicals, BP, Energy Research Centre of the Netherlands	Chemical adsorption	Large laboratory scale/small pilot scale, with large-scale pilot planned for the near future	Hydrotalcite, a naturally occurring aluminum magnesium carbonate hydroxide hydrate.	CO_2-selective hydrotalcite adsorbent is combined with a water–gas shift catalyst and applied to syngas production during natural gas reforming.

PROCESS	DEVELOPER(s)/ SUPPLIER(S)	CLASSIFICATION	STATUS	CHEMICAL(S)	NOTES
Membranes					
Oxygen-Permeable Membranes					
Ion Transport Membrane	Air Products and Chemicals	Membrane	5-ton oxygen/day pilot plant has in operation since 2006. Currently working on 150-ton/day pilot. Scale to 800-ton/day small-commercial unit planned for 2011 and 2000-ton/day by 2013.	Inorganic membrane	This is an oxygen purification system used for air separation.
Oxygen-Selective Polymer Membranes	Various	Membrane	Commercial (to produce 50% O_2)	Polymer membrane	Polymer membranes containing molecular sieves show promise for providing higher-purity O_2 from air.

PROCESS	DEVELOPER(s)/ SUPPLIER(S)	CLASSIFICATION	STATUS	CHEMICAL(S)	NOTES
Membranes for Hydrogen Separation and Integrated Precombustion Systems					
CO_2-Selective Ceramic Membrane for Water–Gas Shift Reactions	Media and Process Technology, the University of Southern California, and National Energy Technology Laboratory	Membrane	Research – laboratory-scale reactor and modeling	Tubular ceramic membrane whose pores are filled with hydrotalcite	This process uses a CO_2-selective ceramic membrane inside a water–gas shift reactor that separates CO_2 from gas produced during coal gasification.
Catalytic Membrane Reactor	Eltron Research and Technology	Membrane	Research – laboratory scale development and testing completed	Layered membrane with 1) ceramic oxide material with methane steam-reforming catalysts, 2) dense perovskite, and 3) a support layer	The membrane operates at high temperature ranging from 850° to 1000°C.
Palladium–Copper Alloy Membrane Reactor	National Energy Technology Laboratory and the Colorado School of Mines	Membrane	Research – laboratory scale	Palladium–copper alloy	Simultaneously catalyzes the water–gas shift reaction and transports hydrogen across the membrane to produce a high-pressure CO_2 stream.
Hydrogen Membrane Reformer	StatoilHydro	Membrane	Research – laboratory-scale demonstration, full-scale conceptual model	Hydrogen-selective membrane	The reactor combines steam reforming, water–gas shift reaction, and hydrogen separation.

PROCESS	DEVELOPER(s)/ SUPPLIER(S)	CLASSIFICATION	STATUS	CHEMICAL(S)	NOTES
HydrogenMembrane Reactor	Dalian Institute of Chemical Physics, SINTEF, National Technical University of Athens, Process Design Center, Energy Research Centre of the Netherlands	Membrane	Research – laboratory scale constructed and tested (25 kW_t)	Pure palladium on a tubular ceramic support	Part of the European CACHET project to develop hydrogen membrane reactors for CO_2 capture.
Inorganic Nanoporous Membrane	Oak Ridge National Laboratory	Membrane	Research – laboratory scale	Three-layer composite inorganic membrane	The inorganic nanoporous membrane removes H_2 from syngas streams, leaving CO_2 as the primary constituent in the gas stream.
High-Temperature Polymeric–Metallic Composite Membrane	Idaho National Energy and Engineering Laboratory, Los Alamos National Laboratory, Pall Corporation, Shell Oil Company	Membrane	Research – laboratory scale	Polybenzimidazole composite layer on a porous stainless steel substrate	For high-temperature hydrogen/CO_2 separation; applies only to gasification-based systems. The process can deliver CO_2 at high pressures.

PROCESS	DEVELOPER(s)/ SUPPLIER(S)	CLASSIFICATION	STATUS	CHEMICAL(S)	NOTES
Palladium-Containing Membrane Reactors	Praxair, T3 Scientific, and CSM United Technologies Research Center and Power+Energy Western Research Institute, Chart Energy and Chemicals, and Synkera Technologies Worcester Polytechnic Institute, Membrane Technology & Research, Siemens Energy America, and T3 Scientific	Membrane	Research – research funding announced in July 2010	Palladium or palladium-based ceramic membranes	These four projects, all funded by DOE National Energy Technology Laboratory, are investigating membrane technology to separate hydrogen and CO_2 from coal-derived synthesis gas.

PROCESS	DEVELOPER(s) /SUPPLIER(S)	CLASSIFICATION	STATUS	CHEMICAL(S)	NOTES
DURING COMBUSTION					
Combustion with Pure Oxygen (without flue gas recirculation)	Various	Other combustion process	Research – pilot scale	Pilot tests done in the past but approach mostly abandoned because of cost and difficulty of construction and maintenance	Combustion temperatures are very high. Requires boilers made with special materials. New construction or major retrofit/rebuild.
Combustion with Pure Oxygen with Flue Gas Recirculation as the Dilution Gas	ALSTOM, ABB, Praxair, Parsons Energy	Other combustion process	Research; currently at pilot scale, with active development and scale-up in progress.	Oxygen	New construction or retrofit. Difficulty with retrofit is eliminating air leakage into boiler, flue, and other flue gas treatment processes.
Chemical-Looping Combustion	ALSTOM, Korean Institute of Energy Research, Vienna University of Technology, Chalmers University	Chemical adsorption	Research to small pilot scale.	Metal oxides used as oxygen adsorbents	Process uses oxygen by metal oxide carriers to combust the fuel, producing CO_2 and water. Condensation of the steam produces a relatively pure stream of CO_2.

PROCESS	DEVELOPER(s) /SUPPLIER(S)	CLASSIFICATION	STATUS	CHEMICAL(S)	NOTES
Advanced Zero Emission Power Process	ALSTOM	Membrane	Research – mathematical modeling – thermoeconomic analysis	Mixed conducting membrane	Replaces the combustion chamber of an ordinary gas turbine with a mixed conducting membrane reactor that separates O_2 from the air for combustion with a fuel (natural gas).
ThermoEnergy Integrated Power System Process	ThermoEnergy Corporation	Other combustion process	Research – patented process		Utilizes high-pressure combustion (700 to 1300 psi) and facilitates the condensation of exhaust components such as water and CO_2 in a condensing heat exchanger.

PROCESS	DEVELOPER(s)/ SUPPLIER(S)	CLASSIFICATION	STATUS	CHEMICAL(S)	NOTES
POSTCOMBUSTION					
Physical Absorption Physical solvent-based absorption processes are typically not used for postcombustion capture because of their low capacity for CO_2 at low pressures.					
Econamine FG^{SM} *and Economine FG Plus*^{SM}	Fluor	Chemical absorption	Commercial for smaller-scale natural gas and coal combustion processes. Scale-up demonstrations planned and in progress.	Monoethanolamine (30 wt% and higher for FG and FG Plus, respectively)	Used in 24 plants around the world, with 10 plants on order. Demonstration facility of >1000 metric tons/day of coal combustion flue gas.
Lummus MEA Absorption Process (aka Kerr-McGee/ABB Lummus Crest process)	Randall Gas Technologies, Inc. (Division of Lummus Technology, a CB&I Company)	Chemical absorption	Commercial for smaller-scale natural gas combustion	Monoethanolamine (15–20 wt%)	Has been commercially applied to capture CO_2 from coke- and coal-fired boilers. Largest plant produces 800 tons/day of CO_2.
KM CDR Process	Mitsubishi Heavy Industries (MHI)	Chemical absorption	Commercial for natural gas combustion flue gas. Scale-up demonstrations are in progress and planned for coal combustion.	Sterically hindered amines (KS-1)	MHI offers performance guarantees for postcombustion for natural gas-fired boilers. Currently working on a large-scale demonstration for coal-fired boilers.

PROCESS	DEVELOPER(s)/ SUPPLIER(S)	CLASSIFICATION	STATUS	CHEMICAL(S)	NOTES
Activated Hot Potassium Carbonate (Benfield, CATACARB, Flexsorb HP, others)	UOP, Eickmeyer & Associates, Exxon Giammarco-Vetrocoke	Chemical absorption	Commercial for gas processing; research is being done on the applicability of related potassium carbonate-based solutions (see IVCAP and piperazine)	Aqueous solution of potassium carbonate with catalysts added to speed the reactions.	Not directly applicable to postcombustion capture because higher feed gas pressures are typically required (see precombustion section of this table). See also the Sargas carbonate process, a high-pressure combustion system that uses a modified Benfield process.
Pilot and Demonstration Scale					
Aker Clean Carbon Mobile Test Unit	Aker Clean Carbon	Chemical solvent absorption	Pilot scale	Various (amines)	Mobile pilot-scale test unit; construction and management of 78,000-ton/year pilot in Mongstad, Norway; planning for full-scale facility in Kårstø, Norway.
Chilled Ammonia Process	ALSTOM	Chemical solvent absorption (with phase change)	Demonstration	Ammonium carbonate	Small- and moderate-scale pilot projects have been completed on coal-fired boiler flue gas. Developing commercial-scale demonstration at 1.5 million tons/year.

PROCESS	DEVELOPER(s)/ SUPPLIER(S)	CLASSIFICATION	STATUS	CHEMICAL(S)	NOTES
Advanced Amine Process	ALSTOM	Chemical solvent absorption	Pilot/small demonstration	Dow UCARSOL™ FGC Solvent 3000 (amine)	Small pilot-scale project on coal-derived flue gas is in progress. Small demonstration facility under development. 20-MW$_{th}$ Front End Engineering Design (FEED) project.
Cansolv CO$_2$ Capture Process	Cansolv Technologies, Inc.	Chemical solvent absorption	Pilot scale	Proprietary amine–amine mixture	A 50-metric-ton/day pilot project is planned. Has been short-listed for the SaskPower Boundary Dam project.
HTC Purenergy Carbon Capture System	HTC Purenergy, Doosan Babcock, University of Regina, Greenhouse Gas Technology Center	Chemical solvent absorption	Pilot scale (?) Company literature indicates availability of 3000-ton/day preengineered modular system. No large-scale pilot projects have been performed to date.	Proprietary amine or mixtures of amines	Amine/amine mixtures developed at the University of Regina in Saskatchewan, Canada. Was selected for Basin Electric Power Cooperative Antelope Valley project (which has been cancelled).
Advanced PCCC Technology	Linde AG with BASF-developed solvents	Chemical solvent absorption	Pilot scale	Proprietary chemical solvent	A 7.2-metric-ton/day pilot plant at RWE Power’s lignite-fired power plant in Niederaussem, Germany, is planned.

PROCESS	DEVELOPER(s)/ SUPPLIER(S)	CLASSIFICATION	STATUS	CHEMICAL(S)	NOTES
ECO_2^{TM}	Powerspan (Powerspan initially licensed an ammonia-based process from the U.S. Department of Energy National Energy Technology Laboratory. They have since switched to a proprietary solvent.)	Chemical solvent absorption	Pilot scale/ Demonstration	Proprietary chemical solvent (originally aqueous ammonia)	Initially ECO_2 was directly linked to Powerspan's electrocatalytic oxidation barrier discharge reactor, which was used to oxidize flue gas pollutants (NO_x, SO_x, Hg) that were then scrubbed using ammonia solutions. Now it is a separate proprietary solvent (probably amine or amine mixture) absorber/stripper system.
$POSTCAP^{TM}$	Siemens, E.ON	Chemical solvent absorption	Pilot scale	Amino acid salts	Pilot-scale project in progress at E.ON power plant near Frankfurt, Germany. Demonstration-scale (280-MW) plant planned for 2015 in Finland. 1-MW slipstream pilot funded by the U.S. Department of Energy for TECO Big Bend Station in Tampa, Florida.

PROCESS	DEVELOPER(s)/ SUPPLIER(S)	CLASSIFICATION	STATUS	CHEMICAL(S)	NOTES
Laboratory Scale					
Ionic Liquids or Room-Temperature Ionic Liquids					
Physical Solvent Room-Temperature Ionic Liquid–Amine Mixture	Ion Engineering, LLC, University of Colorado	Mixed physical solvent and chemical solvent absorption	Research	Physical solvent-type ionic liquid and amine	Proceeding to bench-scale pilot.
Chemical Solvent Room Temperature Ionic Liquids	University of Notre Dame (developer) Other players/ sponsors: U.S. Department of Energy National Energy Technology Laboratory, Air Products and Chemicals, Babcock & Wilcox, DTE Energy, Merck/EMD Chemicals, Trimeric	Chemical solvent absorption	Research	Various	The University of Notre Dame research group has also identified a class of phase-changing compounds that are solid until they react with CO_2 to form an ionic liquid.

PROCESS	**DEVELOPER(s)/ SUPPLIER(S)**	**CLASSIFICATION**	**STATUS**	**CHEMICAL(S)**	**NOTES**
Other Room-Temperature Ionic Liquid Research	Various	Chemical solvent absorption	Research	Various, including imidazolium salts, a special class of ionic liquids that contain high concentration of amine functional groups	Much work is focused on synthesis and/or assessment of ionic liquids. Other studies use these as the basis for making polymer membranes and adsorbents (see membrane and adsorption sections.
Aminosilicones	General Electric Global Research with General Electric Energy and University of Pittsburgh	Chemical solvent absorption	Research	Aminosilicones	Aminosilicones can serve as chemical absorbents for CO_2 in nonaqueous glycol solvent solutions.
Phase-Changing Compounds Several research groups are working on the study of compounds that change phase (solid to liquid or liquid to solid) upon exposure to CO_2.					
Aminosilicone with Phase Change	General Electric Global Research	Phase change (liquid to solid)	Research	Aminosilicones	Some aminosilicones change phases, forming a solid phase upon reaction with CO_2.

PROCESS	**DEVELOPER(s) /SUPPLIER(S)**	**CLASSIFICATION**	**STATUS**	**CHEMICAL(S)**	**NOTES**
Chilled Ammonia Process (has phase change)	ALSTOM	Chemical solvent absorption with phase change	Demonstration	Ammonium carbonate	Chilled ammonia process involves precipitation of solids in the absorber column that are concentrated into a slurry that is pumped to the stripper column for regeneration. Small- and moderate-scale pilot projects completed on coal-fired boiler flue gas. Developing commercial-scale demonstration at 1.5 million tons/year.
Compound that Changes from Solid to Ionic Liquid upon Reaction with CO_2	University of Notre Dame	Phase change (solid to liquid)	Research	Ionic liquid	The University of Notre Dame research group has identified a class of phase-changing compounds that are solid until they react with CO_2 to form an ionic liquid.

PROCESS	DEVELOPER(s)/ SUPPLIER(S)	CLASSIFICATION	STATUS	CHEMICAL(S)	NOTES
Absorption with Catalysis Use of catalysts to increase reaction rates in chemical solvent absorption/stripping has been commercial for as long as chemical solvent absorption has been used. All of the original hot potassium carbonate processes employ “activators” that serve as catalysts.					
Piperazine as a Catalyst for Potassium Carbonate	University of Texas at Austin	Chemical solvent absorption	Research	Potassium carbonate and piperazine	The addition of piperazine accelerates the rate of the CO_2–potassium carbonate reaction. The use of concentrated piperazine without potassium carbonate is also being investigated.
Immobilization of Carbonic Anhydrase	Akermin	Chemical solvent absorption	Research	Carbonic anhydrase in aqueous solutions of amines and/or carbonate salts	Immobilized for transport in a solution (various solvents).
Contained Liquid Permeator and/or Membrane Absorber–Stripper with Carbonic Anhydrase	Carbozyme, Inc.	Membrane-based separation using a chemical solvent solution	Research	Carbonic anhydrase in aqueous solutions of carbonate salts	Immobilized for use in a liquid membrane or membrane absorber/stripper (various solvents).
Enzyme-Enhanced Amines	CO_2 Solution, Inc. with Codexis, Inc.	Chemical solvent absorption	Research	Carbonic anhydrase in aqueous solutions of amines and/or carbonate salts	Immobilized in an absorber or immobilized to carrier for use in an absorber/stripper (various solvents).

PROCESS	**DEVELOPER(s)/ SUPPLIER(S)**	**CLASSIFICATION**	**STATUS**	**CHEMICAL(S)**	**NOTES**
Integrated Vacuum Carbonate Absorption Process (IVCAP)	Illinois State Geologic Survey at the University of Illinois, Urbana–Champaign	Chemical absorption	Research	Carbonic anhydrase is immobilized to a carrier for use in a potassium carbonate solution in a particular process, IVCAP	Employs a potassium carbonate solution to capture CO_2 and uses the enzyme carbonic anhydrase as a catalyst.
Synthetic Catalysts Based on Carbonic Anhydrase Active Site	Partnership between United Technologies Research Center, Lawrence Livermore National Laboratory, the University of Illinois, Babcock & Wilcox	Chemical absorption	Research		This group is developing a synthetic catalyst that is designed to provide the active site of the carbonic anhydrase in a smaller molecule.
Modified Combustion Systems					
Sargas Carbonate Process (pressurized natural gas combustion; pressurized fluidized-bed combustion)	Sargas AS	Pressurized-combustion combined-cycle power generation system with CO_2 capture	Demonstration (1-MW-scale coal demonstration in progress, 100-MW natural gas and 400-MW coal planned)	Potassium carbonate	A high-pressure combustion system using a modified Benfield hot carbonate process. Not applicable for retrofit.

PROCESS	DEVELOPER(s)/ SUPPLIER(S)	CLASSIFICATION	STATUS	CHEMICAL(S)	NOTES
Adsorption					
Overview Study of Physical and Chemical Adsorbents for Postcombustion CO_2 Capture	ADA-Environmental Solutions–DOE funded adsorbent screening study	Adsorption	Research	Various (amines, carbon, zeolites, and carbonates)	Analysis of physical and chemical adsorbents for use in postcombustion capture.
Physical Adsorption Generally not important for postcombustion capture. Physical sorbents can serve as supports for chemical adsorbents or chemical absorbents or be modified to become chemical adsorbents through attachment of appropriate functional groups (i.e., amine functional groups).					
Electrical Swing Adsorption	Oak Ridge National Laboratory University of Porto, Portugal; Centre National de la Recherche Scientifique, Nancy, France University of Queensland, Australia	Physical adsorption and/or chemical adsorption	Research – small bench-scale studies	Activated carbon (monolith or carbon fiber) composite with zeolites	Activated carbon/graphite is used as an electrically conductive support for zeolite molecular sieves that serve as the solid sorbent. A low-voltage current removes the adsorbed CO_2 by resistive heating.
Chemical Adsorption					
Novel Carbon Adsorbent	Advanced Technology Materials, Inc., SRI International	Chemical adsorption with temperature-swing regeneration	Research	Surface-functionalized carbon	Developers plan to develop a moving-bed adsorber/stripper system based on the use of a high-capacity adsorbent.

PROCESS	**DEVELOPER(s)/ SUPPLIER(S)**	**CLASSIFICATION**	**STATUS**	**CHEMICAL(S)**	**NOTES**
Metal Oxides and Metal Hydroxides	National Energy Technology Laboratory	Chemical adsorption	Research	Sodium carbonate, potassium carbonate, magnesium oxide, magnesium hydroxide	Theoretical modeling studies on the use of metal oxides and metal hydroxides as solid adsorbents for postcombustion CO_2 capture.
Stabilized Calcium Oxide Adsorbents	Pacific Northwest National Laboratory	Chemical adsorption	Research	Calcium oxide (CaO) adsorbent with $MgAl_2O_4$ spinel nanoparticles	Targeted for use at high temperature (650°C carbonation and 850°C calcination).
Dry Sorbent-Based Capture Process	RTI International with National Energy Technology Laboratory; Electric Power Research Institute; ARCADIS, Inc.; U.S. Environmental Protection Agency; Sud-Chemie, Inc. Nexant	Chemical adsorption	1-ton/day pilot test, with target commercialization date of 2015	Metal carbonate	CO_2 reacts with lime to form calcium carbonate. Other candidate sorbents include sodium bicarbonate, trona, and potassium carbonate.

PROCESS	DEVELOPER(s)/ SUPPLIER(S)	CLASSIFICATION	STATUS	CHEMICAL(S)	NOTES
Metal Organic Frameworks (MOFs)	UOP, LLC, University of California at Los Angeles, University of Michigan, Northwestern University, Vanderbilt University, University of Edinburgh, and many others	Chemical adsorption	Research	MOFs	Large metal oxide molecules with engineered macromolecular cavities that can adsorb CO_2. They may contain functional groups such as tertiary amines to enhance chemisorption of the CO_2.
Zeolite Imidazolate Frameworks (ZIFs)	Pacific Northwest National Laboratory, University of Pittsburgh	Chemical adsorption	Research	ZIFs	Class of crystalline nanoporous materials made of zeolite minerals and imidazoles at the organic linkages.

PROCESS	DEVELOPER(s)/ SUPPLIER(S)	CLASSIFICATION	STATUS	CHEMICAL(S)	NOTES
Surface-Modified Expanded Mesoporous Silica	University of Ottawa (Developer) and Carbon Capture Technologies, Inc., a branch of CSMG Technologies, Inc. (Licensee)	Chemical adsorbent	Research	Mesoporous silica	Recyclable adsorbents exhibit a high adsorption capacity that is both fast and reversible. Can be used with both wet and dry gas streams.
TDA Dry Solid Sorbent	TDA Technologies, Babcock & Wilcox, Louisiana State University, Western Research Institute	Chemical adsorbent	Research	Alkalized alumina adsorbent	Captures CO_2 at intermediate temperatures and near-ambient pressure. Regenerated using steam.
Novel Amine-Enriched Solid Sorbent	National Energy Technology Laboratory	Chemical adsorbent	Research – laboratory scale	Amine compound grafted onto a carbon support	High sorption capacities with low regeneration energy requirements.

PROCESS	DEVELOPER(s)/ SUPPLIER(S)	CLASSIFICATION	STATUS	CHEMICAL(S)	NOTES
Metal Monolithic Amine-Grafted Zeolite Sorbent	University of Akron, National Energy Technology Laboratory	Mixed absorption/ adsorption	Research	Amine-grafted zeolites plated onto the walls of a metal monolith	Features the novel integration of a metal monolith with amine-grafted zeolites.
Polyionic Liquids	University of Wyoming	Chemical adsorption	Research	Polymers made from ionic liquids	Focus is on the development of polymers referred to as polyionic liquids.
Polymer-Entrapped Ionic Liquids	Georgia Institute of Technology	Mixed absorption/ adsorption	Research	Ionic liquids trapped in hollow fibers made from normal polymers	This “ionic liquid sponge” is used like an adsorbent in a temperature or pressure swing adsorption-type system.
Recyclable CO_2 Adsorbent	University of Ottawa (Developer), Carbon Capture Technologies, Inc., a branch of CSMG Technologies, Inc. (Licensee)	Chemical adsorption	Research	Surface-modified expanded mesoporous silica	Recyclable adsorbents exhibit a high adsorption capacity that is both fast and reversible. Can be used with both wet and dry gas streams.

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Hyperbranched Aluminosilica (HAS)	Georgia Institute of Technology	Chemical adsorption	Research	Amine polymer groups on a silica substrate	Laboratory-scale studies have shown that HAS is reusable, works in the presence of moisture, and can adsorb up to five times as much as other reusable materials.
Membranes					
Polymer Membranes	Various	Selective transport of CO_2 across polymer membranes	Research	Various polymers and polymer composites with adsorbents	*Journal of Membrane Science* September 2010 issue provides excellent coverage of this topic.
Polaris™ Membrane	Membrane Technology & Research (MTR)	Selective transport of CO_2 across polymer membranes	Small-scale pilot	Polymer membrane	Based on a commercial membrane. MTR is also involved in the use of membrane systems for CO_2 separation from natural gas and is investigating the use of its membrane systems for H_2/CO_2 separations.

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Molecular Gate Membrane	Research Institute of Innovative Technology for the Earth – Japan	Selective transport of CO_2 across polymer membranes	Research	Composite polymer membrane	The molecular gate membrane consists of a cardo-polyimide membrane that only allows CO_2 molecules to permeate the membrane, blocking N_2 and H_2 and producing a CO_2-rich stream.
Gelled Ionic Liquids Membranes	University of Colorado	Selective transport of CO_2 across a liquid membrane	Research	Ionic liquid held as a liquid membrane supported in an porous polymer membrane	This research focuses on the development of novel gelled ionic liquid membranes.
Polyvinylidene Fluoride-Based Polymer	RTI International	Selective transport of CO_2 across polymer membranes	Research	Polymer membrane made with polyvinylidene fluoride (PVDF)	This process takes advantage of the specific affinity that the PVDF polymer has for CO_2.
Imidazolium Salt-Based Polymer Membrane	University of Colorado	Selective transport of CO_2 across polymer membranes	Research	Polymerized imidazolium salt ionic liquid compound that forms a structural polymer membrane	Development of polymer membranes based on direct polymerization of a class of ionic liquid compounds known as imidazolium salts.

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Carbozyme Liquid Membrane Permeator	Carbozyme, Inc.	Selective transport of CO_2 across a liquid held between two microporous polymer membranes (enzyme-catalyzed transport)	Research	Aqueous solution of metal carbonate salt and/or amines with immobilized CA	See section on carbonic anhydrase. Carbozyme has also announced development of a membrane-based absorber stripper; see section on other contactors for absorption-based separations.
Other					
Other Contactors for Absorption-Based Separations					
Membrane Contactors Membrane contactors are flat-sheet, spiral-wound, or hollow-fiber membrane modules in which a porous membrane is used to separate the gas phase from an absorption solution. High surface areas reduce the size of the absorber and stripper towers and permit the use of solvent solutions that might not work well in an absorption tower because of the tendency to foam.					
Kvaerner Hybrid Membrane Absorption System	Aker Process Systems (Kvaerner Process Systems)	Alternate absorption contactor – membrane absorber	Pilot scale with Mitsubishi Heavy Industries KS-1 solvent	Microporous polytetrafluoroethylene membranes	Pilot study concluded insignificant capital cost savings and 19% operating cost savings when compared to conventional MEA.

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PoroGen Carbo-Lock Process	PoroGen	Alternate absorption contactor – membrane absorber	Research – laboratory scale, recently funded for 3-year development project	Microporous hollow-fiber polyether ether keytone membranes with fluorocarbon-modified surface.	3-year project includes partnership of PoroGen with Gas Technology Institute and Aker Process Systems.
CATO CO_2 Catcher	TNO	Alternate absorption contactor – membrane absorber	Pilot scale at E.ON Benelux power plant in Rotterdam, Netherlands	Microporous polyolefin membrane used with amino acid salt-based absorbents (CORAL solvents)	
Solvent–Membrane Hybrid Postcombustion CO_2 Capture Process	University of Kentucky	Alternate absorption contactor – membrane absorber	Research – laboratory scale	Microporous membranes with immobilized catalyst	Advanced Project Research Agency-Energy (ARPA–E)-funded project
Carbozyme Proprietary Absorber–Stripper System	Carbozyme	Alternate absorption contactor – membrane absorber	Research – laboratory scale	Microporous membranes with immobilized carbonic anhydrase	See Carbozyme contained-liquid membrane permeator.
Membrane Absorbers	Other researchers	Various – many universities (not detailed with references)	Research and small-scale demonstrations	various	Many university researchers have published work on the use of membrane absorbers for use in capturing CO_2 into solutions of chemical absorbents including metal hydroxides, metal carbonates, and amines.

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Other Novel Absorber Contactors					
Neustream^{TM}-C	Neumann Systems Group, Inc.	Chemical solvent absorption	Development stage for CO_2 capture	Various	A unique horizontal-flow absorber that promises very high mass transfer rates while reducing the overall system footprint and energy consumption.
Cryogenic CO_2 Capture					
Cryogenic Carbon Capture System	Sustainable Energy Solutions	Cryogenic CO_2 capture	Bench-scale project for postcombustion flue gas	Not applicable	Target is postcombustion capture.
Cryogenic CO_2-Capturing System	Cool Energy Ltd.	Cryogenic CO_2 capture	Processing on natural gas – demonstration at 2 million scfd	Not applicable	Target is natural gas processing; may be useful in precombustion capture as well.
Controlled Freeze Zone Process	ExxonMobil	Cryogenic CO_2 capture	Construction of full-scale natural gas-processing facility	Not applicable	Target is natural gas processing; may be useful in precombustion capture as well.

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Mineralization					
Bauxite Waste from Aluminum Refining	Alcoa, Inc.	CO_2 capture by mineralization	Demonstration	Bauxite, alkaline waste from aluminum ore processing	Bauxite waste has a high magnesium content that is reacted with CO_2 to form magnesium carbonate. The neutralized waste is dried and disposed of in a landfill or as fill at the bauxite mine or beneficially used as road base, building materials, or as a soil amendment.
Alkaline Fly Ash-Based CO_2 Capture	Ohio State University	CO_2 capture by mineralization	Laboratory scale	Alkaline fly ash	Flue gas is contacted with alkaline fly ash to form a residual with CO_2 sequestered as a mineral carbonate.
Accelerated Weathering of Magnesium Silicate Minerals	Columbia University	CO_2 capture by mineralization	Laboratory scale	Basaltic ultramafic rocks (high in magnesium)	In nature, CO_2 reacts with minerals such as magnesium silicates over a long period of time to produce a stable precipitate such as magnesium carbonate. Enhanced weathering research is being performed with the goal of accelerating this natural reaction.

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Calera CO_2 Capture Process	Calera Corporation	CO_2 capture by mineralization	DOE and Australian government have funded demonstration projects up to 50-MW equivalent	Fly ash and brines	Combines CO_2 with minerals harvested from waste products including fly ash and/or brines to form usable aggregate and/or cement. Electrochemical methods are used to generate the alkalinity required for mineralizing the CO_2 as a metal carbonate and/or metal bicarbonate.
C-Quest Chemical Sorbent System	C-Quest Technologies	CO_2 capture by mineralization	Laboratory-scale testing	Variety of sorbent ingredients	Makes use of widely available sorbent ingredients that react with CO_2.
SkyMine®	Skyonic Corporation	CO_2 capture by mineralization	"Commercial-scale" demonstration at a cement plant	Brine	Removes CO_2 from industrial waste gas streams through cogeneration of salable carbonate and/or bicarbonate minerals. Electrochemical methods are used to generate alkalinity from the brine.

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New Sky Energy Electrochemical Carbon Capture Technology	New Sky Energy	CO_2 capture by mineralization	Small demonstration unit being constructed	Brine	Utilizes a salt solution and an electrochemical process to make sodium hydroxide (NaOH), which spontaneously combines with CO_2 to produce carbonates such as sodium carbonate and sodium bicarbonate.
Reduction Reduction of CO_2 is the opposite of oxidation. Energy is required to form carbon–carbon and carbon–hydrogen bonds.					
Photosynthetic Reduction					
Photosynthesis – Closed-Environment Agriculture	Warm CO_2 (Terneuzen, The Netherlands); likely others	CO_2 capture by reduction of CO_2	Small-scale commercial	Energy input from sunlight	Waste heat, anhydrous ammonia, and CO_2 are provided to a 1-mi^2 greenhouse facility that grows flowers and food crops.
Photosynthesis – Algae and Microalgae	Various	CO_2 capture by reduction of CO_2	Demonstration	Energy input from sunlight	Some proposed systems use electric lights. When electric lights are used, the process is not economical.

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Algae for Nutritional Supplement	Cyanotech	CO_2 capture by reduction of CO_2	Commercial scale	Energy input for reduction from sunlight.	Small combined heat and power system (2 MW) is used to supply flue gas CO_2 to algae raceways used to grow spirulina that is sold as a nutritional supplement. Approximately 67 tons/month of CO_2 yields 36 tons/month of spirulina in approximately 30 acres of raceway.
Algae for Nutritional Supplement and/or Biofuels	Seambiotic	CO_2 capture by reduction of CO_2	Pilot scale	Energy input for reduction from sunlight	1000-m^2 pilot algae production facility using CO_2 in flue gas from a coal-fired power station in Ashkelon, Israel. Products planned are omega-3 fatty acids and biofuels.
Algae for Biofuels	Pond Biofuels	CO_2 capture by reduction of CO_2	Small pilot scale	Energy input for reduction from sunlight	1500-ft^2 indoor demonstration facility at St. Mary's Cement plant in Ontario, Canada, to produce biofuel.

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Other Biofuels- from-Algae Projects	U.S. Department of Energy NREL (1978–1996), Touchstone Research Laboratory, Phycal Vattenfall project	CO_2 capture by reduction of CO_2	Small-to-medium-size demonstration	Energy input for reduction from sunlight.	Biofuel is the main product. Other products include nutritional supplements for humans and/or fish.
Chemical and Biochemical Reduction					
Production of Polymers	Various	Reduction of CO_2 to form cyclic carbonates or polycarbonates	Commercial use of purified CO_2 is common. Research is being done on the direct use of flue gas as CO_2 source.	Energy input required, typically supplied by other reagents involved in the reaction	The U.S. Department of Energy has funded Novomer Inc. to conduct a study in conjunction with Albermarle Corporation and Eastman Kodak Company to develop novel catalysts and a process to make thermoplastics containing 50 wt% CO_2.
Generation of Electrofuels	Various	Reduction of CO_2 using electrochemical and biochemical processes to make liquid transportation fuels.	Advanced Research Projects Agency-Energy (ARPA-E)-funded research projects	Various	See sections on generation of “Electrofuels” and “STEP Carbon Capture.”