CO$_2$ CAPTURE TECHNOLOGIES

TECHNOLOGY OPTIONS FOR CO$_2$ CAPTURE
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TECHNOLOGY OPTIONS FOR CO$_2$ CAPTURE

Brief description of major technologies for CO$_2$ capture

The main competing technologies for CO$_2$ capture from fossil fuel usage are:
- Post Combustion Capture (PCC) from the flue gas of Combustion-based plants;
- Pre Combustion Capture from the Syngas in Gasification based plants; and
- Oxy Combustion – the direct combustion of fuel with Oxygen.

These three approaches are shown diagrammatically for coal based power systems in Figure 1-1.
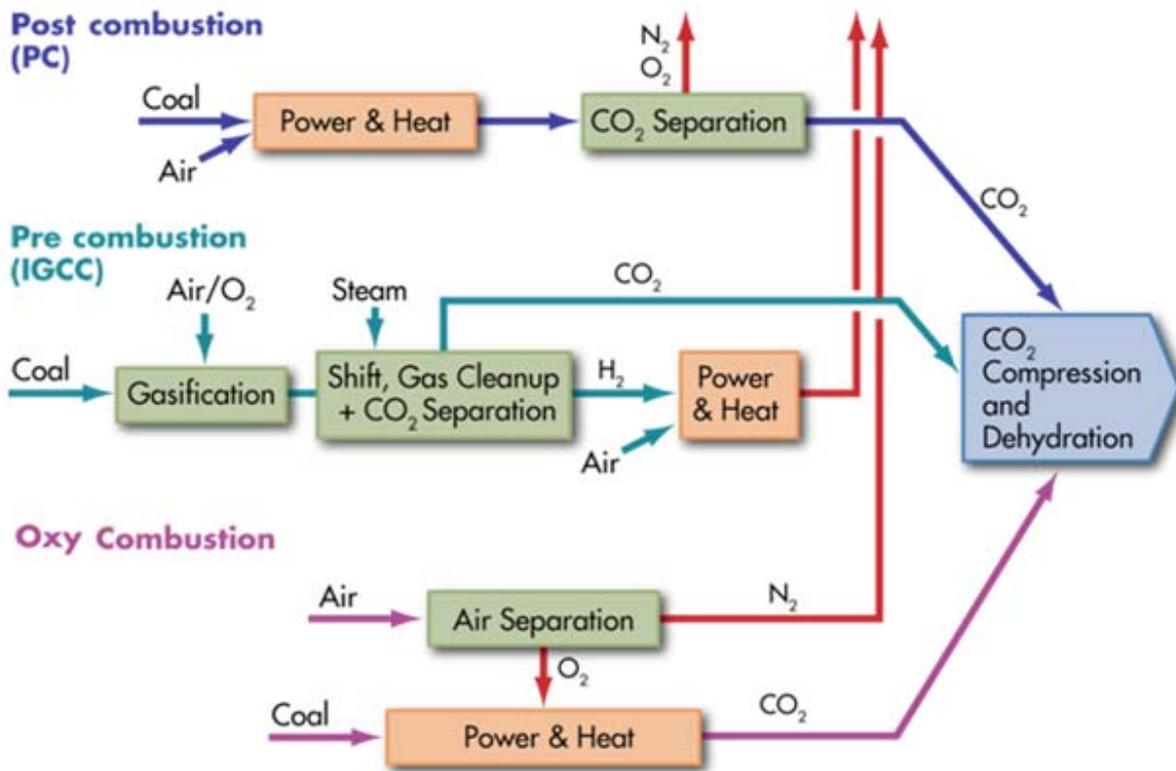
Figure 1-1 Technical Options for CO$_2$ Capture from Coal Power Plants

Post combustion capture (PCC) at near atmospheric pressure can be applied to newly designed plants or retrofitted to existing coal plants after suitable flue gas clean up. Absorption processes are currently the most advanced of the PCC technologies. The PCC technologies can also be used in other industries besides power e.g. cement, oil refining, and petrochemicals.

Pre-combustion capture in the IGCC power application comprises gasification of the fuel with oxygen or air under high pressure, the use of the shift reaction followed by CO$_2$ removal using Acid Gas Removal (AGR) processes with hydrogen rich syngas supplied to the gas turbine based power block. Pre combustion capture can be added to existing IGCC plants but in the future IGCC plants will almost certainly be designed with capture from the start. The pre-combustion capture of CO$_2$ using AGR processes is also practiced commercially in natural gas processing, natural gas reforming and coal gasification plants.

Oxy combustion is the combustion of fuel with oxygen. In an Oxy coal power plant, flue gas is recycled to the oxygen fired boiler to keep the boiler temperature at the level acceptable for boiler tube material integrity. The

flue gas containing mostly CO_2 is purified, dried and compressed. The Oxy technology may also be applied to existing plants but in most cases a new boiler and steam turbine would probably be justified.

Within each of the three major capture categories there are multiple pathways using different technologies which may find particular application more favourably in certain climate conditions, locations, elevations and coal types.

The importance of improved efficiency

The addition of CO_2 capture incurs a very significant loss of efficiency and power output that has a large effect on the LCOE economics since the capital cost has to be spread over less MWh and the fuel cost per MWh is increased. This document is focused on the CO_2 capture technologies and potential improvements to reduce the energy losses and capital costs associated with capture. However, a major contribution to the reduction of CO_2 from fossil based plants will be achieved through increases in the efficiency of the basic technologies of pulverized coal combustion and combustion (gas) turbines.

For example, considerable work is underway to develop and qualify advanced materials that will enable the use of ultra supercritical steam conditions with higher temperatures (up to 700-750°C) and pressures (up to 350 bar). This, in turn, will lead to higher plant efficiencies and lower CO_2 emissions per MWh. As illustrated in Figure 1-2 a 20% reduction in CO_2 emissions can be achieved through efficiency improvement. EPRI studies indicate that this CO_2 emissions reduction from efficiency improvement can be accomplished at lower cost per tonne of CO_2 removed than from CO_2 capture.

For PCC, the major energy losses are incurred in sorbent regeneration and CO_2 compression. Current PCC R&D is focused on improved sorbents that require less energy for regeneration and/or could be regenerated at pressure, thereby reducing the CO_2 compression energy required.
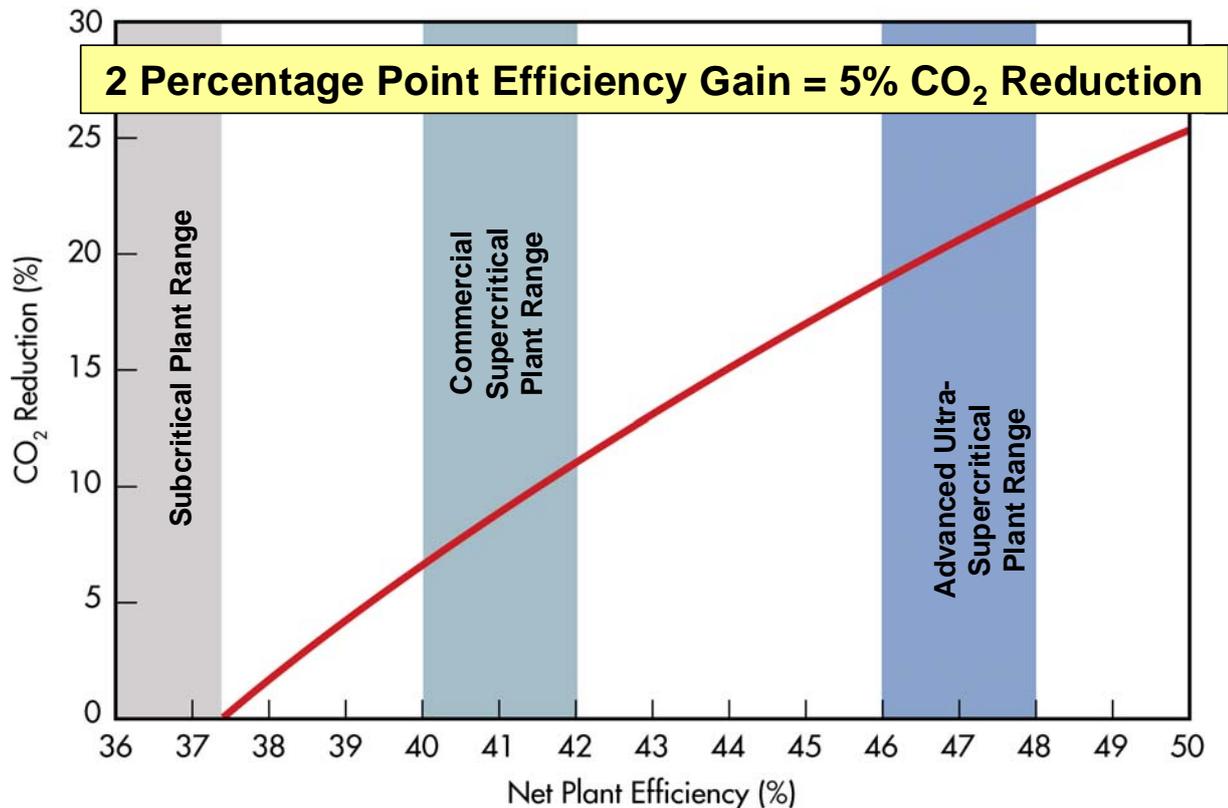

Figure 1-2 PC Plant Efficiency and CO₂ Reduction

There are also major developments underway to increase the firing temperatures (up to 1600°C) and efficiencies of gas turbines. These developments will in turn reduce the CO$_2$ emissions from natural gas combined cycle (NGCC) and Integrated Gasification Combined Cycle (IGCC) plants.

For IGCC pre combustion capture, the major energy losses are incurred in the air separation unit (ASU), water-gas shift, gas cooling and CO$_2$ separation areas. The IGCC R&D is focused on improvements to the ASU, gasification, shift catalysts, and in the processes and equipment that reduce the energy loss of the separation of hydrogen from CO$_2$ and of CO$_2$ compression. The use of higher firing temperature higher efficiency gas turbines will further increase plant efficiency and reduce the CO$_2$ emitted per MWh. These gas turbines will also be of larger sizes that will provide further economies of scale and improve economics.

For oxy combustion the major energy penalty is in the ASU area. Current oxy combustion R&D is focused on energy improvements to the ASU, potential reduction of recycle gas and CO$_2$ purification energy losses. . The use of higher temperature materials in the boiler and steam turbine will further increase efficiency and reduce the CO$_2$ emitted per MWh.

Technology readiness level (TRL)

Throughout this chapter the term Technology Readiness Level (TRL) will be used to indicate the development level of the technologies described. The following outline of the TRL concept has been mostly taken from the Global CCS Institute Report #4 of the Strategic Analysis Series.

This TRL approach can be particularly useful in tracking the status of individual technologies throughout the stages of the R&D timeline. The nine TRLs are listed in Table 1-1.

The achievement of a given TRL will inform process developers and organizations of the resources required to achieve the next level of readiness. An achievement of TRL-9 indicates that the first successful operation at normal commercial scale has been achieved and that the technology can be deployed with risks that are comparable to those undertaken on other commercial technologies. Progressively higher technical and financial risks are required to achieve the TRLs up to and including TRL-9.

Table 1-1 The nine technical readiness levels

TRL-9	Full-Scale Commercial Deployment
TRL-8	Sub-Scale Commercial Demonstration Plant (>25% commercial scale)
TRL-7	Pilot Plant (>5% commercial scale)
TRL-6	Component Prototype Demonstration (0.1-5% of full scale)
TRL-5	Component Prototype Development
TRL-4	Laboratory Component Testing
TRL-3	Analytical, 'Proof of Concept'
TRL-2	Application Formulated
TRL-1	Basic Principles Observed

More detailed information on the background justification for the TRL rankings in this document are included and discussed in the separate sections of this document that cover each of the three major capture pathways.

While the actual TRL levels of technologies and sectors have not changed since 2009 there has been significant progress towards higher TRL in most areas.

Commercial demonstration of advanced coal technologies

The development of emission controls on coal fired power plants can be used as an example of technology progression through the required TRLs. In the mid-20th century, coal-fired power plants had limited controls for sulphur dioxide (SO$_2$), nitrogen oxides (NOx) or mercury emissions. Throughout the past 50 years, various technologies to control these pollutants have progressed from about TRL-4 to full commercial availability. This experience has shown that the achievement of TRL-9 can take approximately 20 or more years. This long development period is largely dictated by costs, design, construction and operational testing activities associated with the pilot plants (to achieve TRL-7), sub-scale commercial demonstration plants (to achieve TRL-8) and the first full-scale, commercial deployment (TRL-9).

EPRI comments

The use of TRL in the context of advanced coal technologies has some drawbacks. The TRL classification system was devised by NASA to assess technology readiness only. It was not designed to address 'economic' readiness. Thus, a technology may reach TRL-9 and be technically mature and still not meet project economic requirements. The TRL system does not address the economic feasibility of deploying the technology.

In the past few years, 'full scale' coal-fired power plants purchased by utilities have a net capacity exceeding 400 MWe and largely greater than 600 MWe. For the purposes of a TRL assessment of advanced coal technology, it is suggested that TRL-9 would be achieved by a power plant in the capacity range 400-800 MWe (net). By this metric, successful operation of the Kemper County (524 MWe) would achieve TRL-9, albeit at a CO$_2$ capture rate less than the 90% commonly imagined. Successful operation of Boundary Dam (110 MWe) and FutureGen (200 MWe) would achieve TRL-8: sub-scale commercial demonstration plant. Technology suppliers to Boundary Dam and FutureGen may claim 'commercial' operation, but it would be operation at a scale significantly less than that commonly purchased by utilities.

Integrated CCS demonstration is crucially needed

Although current technology needs further improvements, it is extremely important to demonstrate CCS on a commercial scale as soon as possible. This is needed for the demonstration of capture technology operating in an integrated mode in a real power plant and in a real power grid environment. It is also necessary to demonstrate sequestration/storage at sufficient scale that has credibility for further deployment. Unless progress is made at the commercial CCS demonstration scale to answer these two basic issues it will become increasingly difficult to justify continued R&D funding on potential improvements to capture and storage technologies.

If multiple CCS demonstrations with improved technologies are to be achieved at large-scale (i.e., TRL-9) by 2020 to proceed with commercial deployment, then many technologies need to be approaching the pilot plant stage (TRL-7) today. However, currently there are very few organizations funding demonstrations at one-tenth to full commercial-scale. Some pilot plant scale capture projects have been funded but advancing to sub-commercial scale demonstrations and larger will require an order of magnitude greater level of funding.

The total capital cost of investment for PCC demonstration would be significantly lower if PCC was retrofitted to an existing coal plant than if a new SCPC with PCC was constructed. However, the technical risk is probably not very different from that associated with a newly built SCPC with PCC. PCC retrofit to an existing plant will also incur a loss of power output of perhaps 30% so that replacement power may be needed.

Commercial deployment of CCS technology

Sub-scale commercial demonstration projects are being developed in the US and Europe and the Boundary Dam PCC plant is under construction. The initial integrated full scale commercial sized CCS coal based demonstration projects will only proceed with significant government support. The Kemper County IGCC plant is currently the only full scale CCS plant that is fully funded and in construction. While integrated commercial CCS demonstration projects are clearly a pre-requisite, full scale commercial deployment will only proceed is

there is a value attributable to the reduction of CO$_2$ emissions (or possible sale) and that CCS is found to be a competitive abatement choice.

It can be noted that some pre combustion and post combustion capture industrial projects have been able to proceed because of the value attributable to the sale of the CO$_2$ for EOR.

Advantages and disadvantages of major CO$_2$ capture technologies

Post combustion capture advantages

- Can be retrofitted to existing plants allowing the continued operation of valuable resources
- In either new build or retrofit application it enables the continued deployment of the well established Pulverized Coal (PC) technology familiar to power industries worldwide
- The continued development of improved materials for Ultra Supercritical (USC) plants will increase the efficiency and reduce the CO$_2$ emissions of future PC plants
- The widespread R&D on improved sorbents and capture equipment should reduce the energy penalty of PCC capture
- Sub-scale demonstration of PCC is proceeding. The 110 MW Boundary Dam project of Saskatchewan Power with PCC using the Cansolv process is under construction with planned operation in 2014.

Post combustion capture challenges

- Amine processes are commercially available at relatively small scale and considerable re-engineering and scale-up is needed
- The addition of capture with current amine technologies results in a loss of net power output of about 30% and a reduction of about 11 percentage points in efficiency. In the case of retrofit this would imply the need for replacement power to make up for the loss.
- Most sorbents need very pure flue gas to minimize sorbent usage and cost. Typically < 10 ppmv or as low as 1 ppmv of SO$_2$ plus NO$_2$ is required depending on the particular sorbent
- Steam extraction for solvent regeneration reduces flow to low-pressure turbine with significant operational impact on its efficiency and turn down capability.
- Water use is increased significantly with the addition of PCC particularly for water cooled plants where the water consumption with capture is nearly doubled per net MWh. For air cooling the water consumption is also increased with capture by about 35% per net MWh.
- Plot space requirements are significant. The back-end at existing plants is often already crowded by other emission control equipment. Extra costs may be required to accommodate PCC at some more remote location.

Pre combustion capture advantages

- Pre combustion capture using the water-gas shift reaction and removal of the CO$_2$ with AGR processes is commercially practiced worldwide.
- Pre combustion capture of the CO$_2$ under pressure incurs less of an energy penalty (~20%) than current PCC technology (~30%) at 90% CO$_2$ capture.
- Ongoing R&D on improved CO shift catalysts, higher temperature gas clean up and membrane separation technology for hydrogen and CO$_2$ has the potential to produce a step-change reduction in the energy penalty of capture
- Water use, while still substantial, is lower than with PCC
- The ongoing continued development of larger more efficient gas turbines can markedly improve the efficiency of future IGCC plants
- The Kemper County plant in Mississippi, an IGCC plant with pre combustion capture, is under construction with planned operation in 2014.

Pre combustion capture challenges

- While the energy loss with addition of pre-combustion capture is lower than with the addition of PCC the energy loss is still significant
- The commercial demonstration of large F or G gas turbines firing hydrogen has yet to be demonstrated in an IGCC plant with capture
- In the event of a need to vent the CO$_2$ additional purification may be needed
- IGCC is not yet very widely used in the power industry
- The capital costs of IGCC without capture are much higher than SCPC without capture. The IGCC costs need to be reduced to compete more effectively.

Oxy combustion advantages

- Oxy-combustion power plants should be able to deploy conventional, well-developed, high efficiency steam cycles without the need to remove significant quantities of steam from the cycle for CO$_2$ capture.
- The added process equipment consists largely of rotating equipment and heat exchangers; equipment familiar to power plant owners and operators. (No chemical operations or significant on-site chemical inventory).
- Ultra-low emissions of conventional pollutants can be achieved largely as a fortuitous result of the CO$_2$ purification processes selected, and at little or no additional cost.
- On a cost per tonne CO$_2$ captured basis, it should be possible to achieve 98+% CO$_2$ capture at an incrementally lower cost than achieving a baseline 90% CO$_2$ capture.
- Development of chemical looping combustion with advanced ultra-supercritical steam cycles could result in an oxy-combustion power plant (with CO$_2$ capture) that is higher efficiency than air-fired power plants being built today (without CO$_2$ capture).
- The best information available today (with the technology available today) is that oxy-combustion with CO$_2$ capture should be at least competitive with pre- and post-combustion CO$_2$ capture and may have a slight cost advantage.

Oxy combustion challenges

- It is not possible to develop sub-scale oxy-combustion technology at existing power plants. An oxy-combustion power plant is an integrated plant and oxy-combustion technology development will require commitment of the whole power plant to the technology. Thus, the technology development path for oxy-combustion may be more costly than that for either pre-combustion or post-combustion capture which can be developed on slip streams of existing plants.
- The auxiliary power associated with air compression in a cryogenic air separation unit and CO$_2$ compression in the CO$_2$ purification unit will reduce net plant output by up to 25% compared to an air fired power plant with the same gross capacity (without CO$_2$ capture).
- There is no geological or regulatory consensus on what purity levels will be required for CO$_2$ compression, transportation and storage. For this reason, most oxy-combustion plant designs include a partial condensation CO$_2$ purification system to produce CO$_2$ with purity comparable to that achieved by amine post combustion capture. Oxy-combustion costs may be reduced if the purity requirements could be relaxed.
- Air-fired combustion is commonly anticipated for start-up of oxy-combustion power plants. The very low emissions achieved by oxy-combustion with CO$_2$ purification cannot be achieved during air-fired start-up operations without specific flue gas quality controls for air-fired operations that are redundant during steady state oxy-fired operations. If a significant number of annual restarts are specified, either these added flue gas quality controls will be required (at additional capital cost) or provisions must be made to start up and shut down the unit only with oxy-firing and without venting significant amounts of flue gas.
- Plot space requirements are significant for the air separation unit and CO$_2$ purification units.

ACRONYMS AND SYMBOLS

AFBC	Atmospheric Fluidized Bed Combustion
AGR	Acid gas removal
AQCS	Air Quality Control System
ASU	Air Separation Unit
B&W	Babcock & Wilcox
Bara	Bars absolute
Barg	Bars gauge
BFW	Boiler feedwater
BP	British Petroleum
Btu	British thermal unit
CC	Combined Cycle
CCGT	Combined Cycle Gas Turbine
CCPI	Clean Coal Power Initiative
CCS	CO$_2$ capture and Storage (or Sequestration)
CCT	Clean Coal Technology
CF	Capacity Factor
CFB	Circulating fluidized bed
CHP	Combined Heat and Power
CO$_2$	Carbon dioxide
COE	Cost of electricity
COP	ConocoPhillips
CT	Combustion Turbine
DOE	U. S. Department of Energy
DOE NETL	Department of Energy National Energy Technology Laboratory
ECUST	East China University of Science and Technology
EEPR	European Energy Programme for Recovery
EIA	Energy Information Administration
EOR	Enhanced Oil Recovery
FBC	Fluidized-bed combustion/combustor
FEED	Front End Engineering Design
FGD	Flue gas desulphurization
FOAK	First of a kind
F-T	Fischer Tropsch
ft^3	Cubic feet
FW	Foster Wheeler
FWI	Foster Wheeler Italiana
GHG	Greenhouse Gas
GI	Gasification Island
GJ	Gigajoule
gpm	Gallons per minute (US)
GT	Gas Turbine
H$_2$S	Hydrogen sulfide
HgA	Mercury absolute
HHV	Higher heating value
HRSG	Heat recovery steam generator
HP	High pressure
IEA	International Energy Agency
IGCC	Integrated Gasification Combined Cycle
IP	Intermediate pressure
IPP	Independent power producer
kJ	Kilojoules
KBR	Kellogg, Brown & Root

LCA	Life Cycle Analysis
LCOE	Levelized Cost of Electricity
LHV	Lower heating value
LP	Low pressure
LSTK	Lump Sum Turnkey
mt	Metric ton
MDEA	MethylDiethanolamine
MMBtu	Million Btu
MPa	Mega Pascal
MTG	Methanol to Gasoline
MTO	Methanol to Olefins
NCCC	National Carbon Capture Center
NDRC	National Development and Reform Commission (China)
NETL	National Energy Technology Laboratory
NGCC	Natural Gas Combined Cycle
NH_3	Ammonia
Nm^3	Normal cubic meters
NO_X	Nitrogen oxides
NSPS	New Source Performance Standards
OCGT	Open Cycle Gas turbine
O&M	Operation and maintenance
PC	Pulverized Coal
PCC	Post Combustion Capture
ppmv	parts per million by volume
PRB	Powder River Basin (Coal)
PSDF	Power System Development Facility
psia	Pounds per square inch absolute
psig	Pounds per square inch gage
R&D	Research & Development
RD&D	Research, Development and Demonstration
RQ	Radiant Quench (GE)
RTI	Research Triangle Institute
RWE	Rheinische Westphalien Electricidadeswerke
SCFD	Standard Cubic Feet per day
SNG	Substitute Natural Gas
SCPC	Supercritical Pulverized Coal
SCR	Selective catalytic reduction
SO_2	Sulphur dioxide
SRU	Sulphur Recovery Unit
st	Short ton (2000 pounds)
stpd	Short tons per day
TCR	Total Capital Requirement
TFC	Total Field Cost
TPC	Total Plant Cost
USC	Ultra Supercritical
US EPA	US Environmental Protection Agency
WGCU	Warm gas clean up

CO₂ CAPTURE TECHNOLOGIES

PRE COMBUSTION CAPTURE
JANUARY 2012

CONTENTS

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PRE COMBUSTION CAPTURE

Introduction

The oil, gas and chemical industries have been separating CO$_2$ from gas streams for decades. In most cases the CO$_2$ is removed in order to meet the required downstream product requirements, whether natural gas, hydrogen or chemicals. The term pre-combustion capture has come into use relatively recently mostly in the context of gasification based power plants, particularly IGCC, where, in anticipation of requirements to limit CO$_2$ emissions, plant designs have been developed to convert the gas produced from gasification (henceforth referred to as 'syngas') to hydrogen and CO$_2$ and to remove the CO$_2$ from the syngas stream prior to the combustion of the hydrogen rich gas in the gas turbine.

Pre Combustion Capture Technology[1]

In natural gas processing, natural gas reforming, gasification and IGCC the ultimate capture of the CO$_2$ is currently accomplished under pressure by an acid gas removal (AGR) process of absorption in a solvent followed by regenerative stripping of the rich solvent to release the CO$_2$ which with subsequent compression can be sent to sequestration or supplied for EOR.

There are two major generic types of 'acid gas' (i.e., CO$_2$, H$_2$S, COS) removal (AGR) solvents – chemical and physical.

Chemical Absorbents

Chemical absorbents (e.g., MDEA and other amines) <u>react</u> with the acid gases and require heat to reverse the reactions and release the acid gases. These processes generally have lower capital for AGR than physical solvents, but use larger amounts of steam-heat for solvent regeneration.

Physical Absorbents

Physical absorbents (e.g., Selexol, Rectisol) <u>dissolve</u> acid gases preferentially with increasing pressure. The absorbed acid gases are released from the solvent when pressure is decreased and temperature is increased. Significantly less steam-heat is required for solvent regeneration than with chemical solvents. The Rectisol process, which uses chilled methanol, generally has a higher capital cost, but provides the most complete removal.

The pre-combustion removal of CO$_2$ from syngas has some thermodynamic advantages over PCC. Natural gas processing, reforming and gasification are conducted under pressure (typically > 40 bar) where the higher partial pressure of CO$_2$ enables the use of a physical solvent (e.g. Selexol) that enables some of the CO$_2$ to be regenerated at pressure through a series of flash drums thereby reducing the auxiliary power required for CO$_2$ compression. The efficiency penalty for adding PCC to SCPC is 10-11% points in efficiency whereas the penalty for the addition of pre combustion capture to an IGCC is generally 7-8% points.

A generic process flow diagram for the acid gas removal section of an IGCC plant designed for CO$_2$ capture is shown in Figure 3-1. The first absorber/stripper section is for the removal of a H$_2$S-rich stream that is usually sent to a Claus unit for recovery of elemental sulphur for sale. The sulphur free gas is then sent to a second absorber for removal of the CO$_2$ and the hydrogen rich syngas is sent to the gas turbine power block. The CO$_2$ rich solvent is sent to a stripper for solvent regeneration and the stripped CO$_2$ is dried and compressed for transportation and storage.

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[1] Engineering Economic Evaluations of Advanced Coal Technologies with Carbon Capture and Storage -2011. EPRI Report #1022025. G. Booras June 2011
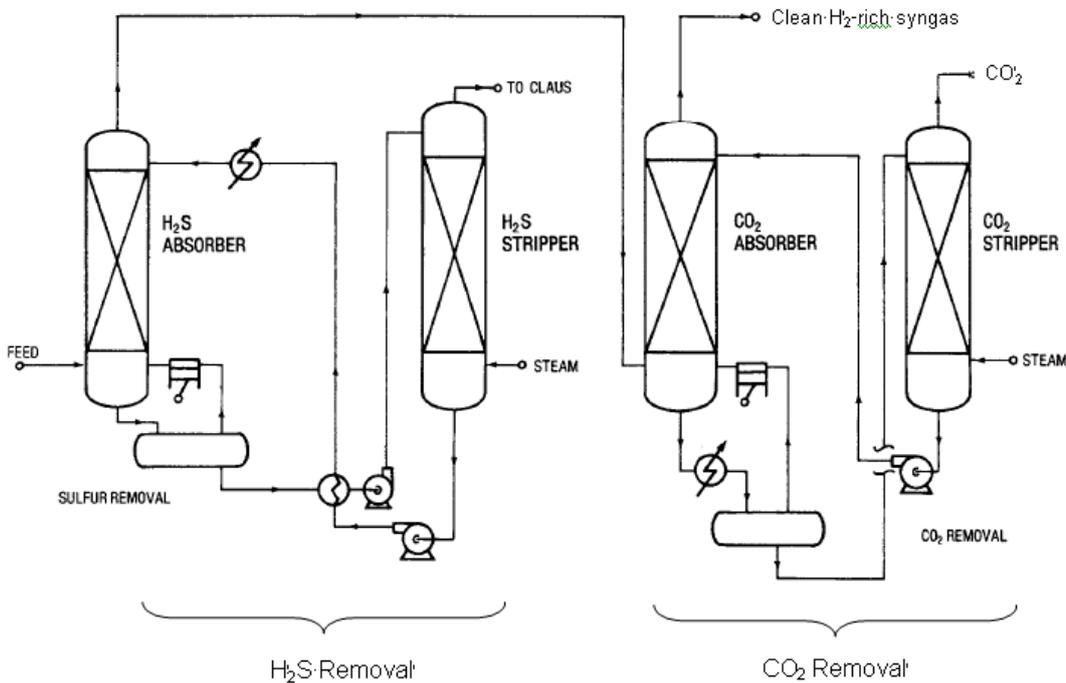
Figure 3-1 Typical IGCC AGR Process Arrangement for CO$_2$ Capture

Typically all the solvents can accomplish >90% CO$_2$ removal, but the overall percentage of capture depends on the amount of water-gas shift conducted. For a 600 MW IGCC plant the space requirements for the water-shift reactor(s), CO$_2$ removal, drying, and compression are similar for all solvent options, about 0.6-0.8 hectares.

Pre-Combustion Capture Applications

CO$_2$ Capture from Natural Gas

Much of the World's sources of natural gas contain CO$_2$ and Hydrogen Sulfide (H$_2$S). The H$_2$S, and in many cases the CO$_2$, must be removed to meet the purity requirements of natural gas pipelines and for the production of Liquefied Natural Gas (LNG). The H$_2$S and CO$_2$ can each be removed separately or together (bulk removal) from the natural gas through the use of one of several commercially available AGR processes. At most of the currently operating natural gas processing plants the H$_2$S is converted to elemental sulphur for sale and the captured CO$_2$ is vented. However there are several projects where the CO$_2$ is compressed for sequestration or for use in Enhanced Oil Recovery (EOR).

CO$_2$ Capture from Natural Gas Reforming and Partial Oxidation

Three processes - Steam Methane Reforming (SMR), Autothermal Reforming and Partial Oxidation (with oxygen) - are widely used commercially for the production of hydrogen and chemicals such as ammonia, methanol etc from natural gas. These processes can also be used with refinery gas, propane, butanes or naphtha as the feed. All three processes produce a syngas containing hydrogen, carbon monoxide (CO), CO$_2$ and excess steam which is cooled and passed through a catalyst bed where the CO is reacted with steam to produce hydrogen and CO$_2$ (known as a shift reactor which produces shifted syngas) The CO$_2$ can then be removed from the shifted syngas by using currently commercially available AGR processes. Most of the CO$_2$ from these plants is currently vented. However in plants that produce hydrogen for ammonia manufacture the co-produced CO$_2$ is sometimes used to react with ammonia to produce urea.

There are a few projects in operation and others being considered where the CO$_2$ removed from natural gas reforming or partial oxidation is compressed and used for sequestration or EOR.

CO$_2$ Removal from Coal Gasification Plants

CO$_2$ removal from coal gasification derived syngas is a mature commercial process widely practiced throughout the world. A couple of coal gasification plants are noted that are currently capturing CO$_2$ for use in EOR.

The gasification of coal, petroleum coke and heavy oils with oxygen are in widespread commercial use for the production of chemicals such as ammonia, urea, methanol, dimethyl ether, SNG, gasoline and other transportation fuels via the Fischer Tropsch process. In these plants the produced syngas is cleaned of particulate matter and subjected to the shift reaction to produce the appropriate CO/H$_2$ ratio for subsequent synthesis. The sulphur in the feedstock is converted to H$_2$S and carbonyl sulphide (COS). Commercial shift catalysts are available for use on either sulphur containing syngas (sour gas) or on sulphur free syngas (sweet gas).

With sour gas the shift catalyst will also convert the COS to H$_2$S. The H$_2$S and CO$_2$ can each be removed separately or together (bulk removal) from the shifted syngas through the use of one of several commercially available AGR processes. An alternative process scheme is the removal of the sulphur species from the syngas by COS hydrolysis followed by an AGR process before conducting the shift reaction on the sweet (i.e. sulphur free) syngas.

IGCC Design Options for CO$_2$ Capture

There are several IGCC plants in operation in several countries but to date none of them has incorporated CO$_2$ capture. However several IGCC projects that include capture are being developed and there is one project, the Kemper County project in Mississippi, that is in construction.

In an IGCC plant, CO$_2$ capture is accomplished as previously described for gasification plants. One or two stages of water-gas shift are used on the particulate free syngas and the addition of steam may be necessary dependent on the specific gasification technology employed. This is followed by gas cooling and the separate removal of H$_2$S and CO$_2$ in two AGR absorption/stripping units arranged in series. The H$_2$S rich stream usually is fed to a Claus plant (sulphur recovery unit or SRU) and the CO$_2$ is dried and compressed for sequestration or use in EOR. Tail gas from the SRU can be recycled to the AGR inlet to improve CO$_2$ recovery. CO$_2$ capture may be added as a retrofit or included in the design of a new plant. Figure 3-2 is a block flow diagram of IGCC with CO$_2$ capture. It shows the typical IGCC arrangement for oxygen blown gasification processes. However the MHI and the Southern Company's TRIG^{TM} processes are both air blown. For these air blown processes the Air Separation Unit (ASU) is essentially replaced with an additional main air compressor to augment the air extracted from the gas turbine compressor as air supplied to the gasification island.

In an IGCC plant with CO$_2$ capture the syngas fuel to the gas turbine is mostly comprised of hydrogen, typically diluted with nitrogen. Although the CO$_2$ capture process from gasification syngas is a mature commercial technology, hydrogen firing in large F Class gas turbines and the whole IGCC plant operation incorporating capture in an integrated manner has yet to be demonstrated.
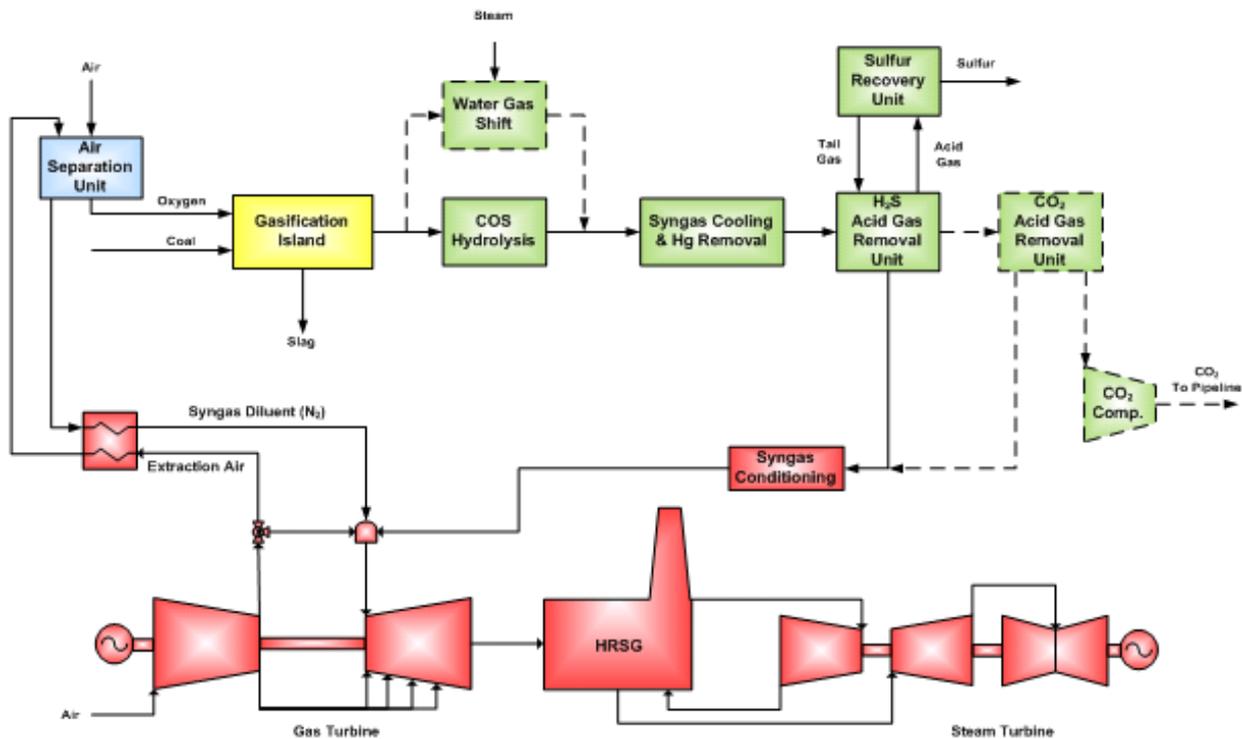
Figure 3-2
Process Flow Diagram of Generic IGCC Plant Showing Retrofit Modifications for CO$_2$ Capture

IGCC Retrofit Addition of Capture

There are a few IGCC plants in operation without capture however prospectively most IGCC projects will almost certainly plan to incorporate capture in the original design.

If CO$_2$ capture was to be added to an IGCC design that did not envisage the future addition of capture there are additional cost and performance penalties over a new built plant with capture. The addition of the shift reactor results in less syngas energy being delivered to the power block. It also results in a higher syngas flow to the AGR section so that additional absorber capacity will be needed.

Additional ASU, Gasification and gas clean-up capacity will be needed to fully load the gas turbines when Shift is added. If this oversizing is included in the initial IGCC investment this version of 'capture ready' would then permit full gas turbine output with hydrogen when capture is added.

Addition of sour shift increases gas flow to the AGR by 45-60% (particularly for the dry coal fed gasifiers with high CO content). The AGR would be unable to take the extra flow unless there was pre-investment oversizing. It may therefore be necessary to add a parallel absorber or replace the entire AGR plant (with a new two column absorption system) if capture is to be added to an existing IGCC designed without capture.

Alternatively the original AGR (focused on H$_2$S Removal) could be retained and a Sweet shift added after the AGR with a simpler bulk CO$_2$ removal AGR (ADIP, MDEA, Selexol) added after shift. This would minimize intrusion into existing plant. This trade off of Sour versus Sweet Shift needs to be examined and may differ among the different gasification Technologies. Sweet shift may incur additional efficiency and output penalties. Quench type gasifiers would probably favour the use of sour Shift.

Pre-Combustion Capture – Current Status and Technology Providers

TRL of Current IGCC Designs with Capture

There are several commercial sized IGCC projects with capture in and one (Kemper County) under construction. However, the designs of IGCC plants incorporating capture using current capture technology incur high energy losses of 7-8% points through the addition of capture. The energy losses occur in many parts of the IGCC flow scheme.

For an IGCC plant with capture based on current technology, the TRL of the major components of the ASU, gasification, gas cooling, shift, sulphur removal and CO_2 capture are all at TRL 9.

TRL of Pre-Combustion Capture in other Applications

The capture of CO_2 from natural gas processing, natural gas reforming and coal gasification is commercially practiced worldwide (i.e. TRL 9). In a few plants the captured CO_2 is being sequestered or used for EOR.

Leading Providers of IGCC Technology

The leading providers of gas turbine based power blocks for the IGCC application with capture are General Electric, Siemens and MHI. Each of these companies can also provide gasification technologies so that they are in a good position to supply overall IGCC technology packages when linked with ASU, shift and AGR technology providers.

The leading providers of the various IGCC component technologies described in this Section are listed in Table 3-1.

Table 3-1 Leading Providers of IGCC Component Technologies

Technology	Leading Provider Companies
Air Separation	Air Products, Praxair, Air Liquide, Linde
Gasification	Heavy Oil – General Electric, Shell, Lurgi,
	Fixed Bed – Lurgi/Air Liquide FBDB, Envirotherm BGL
	Fluid Bed - Southern/KBR TRIG™, Uhde - HTWinkler, SES U Gas, HRL IDGCC
	Entrained Flow - General Electric, ConocoPhillips E Gas™, ECUST, Shell, Siemens, Uhde, MHI (Mitsubishi Heavy Industries)
Shift	Haldor Topsoe, Sud Chemie, Johnson Matthey
Acid Gas Removal	Dow and BASF (MDEA), UOP (Selexol), Lurgi/Air Liquide and Linde (Rectisol), Shell (Sulfinol, ADIP).
Gas Turbines	General Electric, Siemens, MHI

Leading Current Providers of AGR Processes for CO₂ Capture

The leading suppliers of AGR processes are Dow and BASF for MDEA, UOP for Selexol, Lurgi/Air Liquide and Linde for Rectisol, Shell for Sulfinol and ADIP.

Pre-Combustion CO₂ Capture – Challenges/ Future Direction

Although the efficiency loss of 7-8 percentage points for addition of capture to IGCC is currently less than for PCC with MEA in SCPC, it is still very high. The major thrust in RD&D for IGCC designs with capture is to reduce the energy penalty. While the additional capital cost of capture equipment is not insignificant it is net power output loss that is the most significant economic detriment of capture addition.

CO$_2$ Capture at Warm or Hot Gas Temperature[2]

Current AGR processes operate at low temperatures below 40°C. Cooling the syngas to that temperature condenses water from the syngas with an accompanying loss of energy and mass. If the AGR could be accomplished at a higher temperature (e.g. at the temperature of the outlet of the shift reactor) there would be lower energy losses and more motive mass to the gas turbine.

RTI is developing a process for the removal of sulphur species from syngas at temperatures > 230°C using a zinc oxide based sorbent in a transport type reactor with oxidative regeneration of the loaded sorbent. This has been tested at small scale on a slipstream at the Eastman gasification plant in Kingsport, TN and a larger scale unit is to be installed and tested on a 50 MW equivalent slip stream at the Tampa Electric IGCC plant in Florida.

However to take full advantage of this process there must also be processes for the hot removal of trace contaminants (Cl, As, Hg etc) and CO$_2$. The Benfield and CataCarb processes that use a solution of Potassium Carbonate are possible candidates however the sorbent regeneration is at atmospheric pressure.

A more promising approach is the use of a high temperature membrane that could potentially separate hydrogen and CO$_2$ while producing each at relatively high pressure.

Membrane Separation of Hydrogen and CO$_2$

The Eltron high temperature metallic membrane for hydrogen transport has had some success at a small scale. Eastman Chemical has been brought on as a partner and a scale up is planned at the Eastman gasification site. This technology has the potential of incorporating the shift catalyst in its design. A preliminary EPRI evaluation of this technology, when preceded by RTI's warm gas clean-up process (using Zinc oxide), showed significant improvement in efficiency. The ability to produce both the hydrogen and CO$_2$ at pressure results in reduced auxiliary power demand.

Another type of membrane is being developed by MTRI (Membrane Technology Research Inc) for testing on syngas at the NCCC (National Carbon Capture Center). The US DOE is supporting both Eltron and MTRI in their membrane process development. These membrane technologies are considered to be at TRL (Technical Readiness Level) 4 to 5.

Other Processes for Separation of Hydrogen and CO$_2$

The use of chilled ammonia and cryogenic processes for CO$_2$ capture are being studied and have the potential to produce the captured CO$_2$ at pressure thereby reducing the auxiliary power load. An ammonium carbonate – ammonium bicarbonate (AC-ABC) process is being developed, under DOE-NETL funding, by Stanford Research Institute (SRI) for pre-combustion capture of CO$_2$. SRI had previously conducted some of the initial experimental work using the same AC-ABC system for post combustion CO$_2$ capture that formed the basis for the Alstom chilled ammonia PCC process. The pre combustion AC-ABC process is at about TRL 4-5. The use of a cryogenic process for the pre-combustion removal of CO$_2$ by chilling the shifted syngas stream has also been proposed but not yet tested. This is considered to be at TRL 2 to 3.

Energy Losses in IGCC with Capture and RD&D Needs[3]

Although there is additional capital involved, the largest component of the poor economic performance in pre-combustion capture systems is the loss of energy involved. Much of the RD&D effort is aimed at reducing the energy losses due to capture in the various process steps but one of the greatest improvements to the overall IGCC technology is the development of high firing temperature larger gas turbines of higher efficiency. This

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[2] Evaluation of Potential Improvements in IGCC Pre-combustion CO$_2$ Capture. EPRI Report # 1021640. A.Bhown, N.Holt December 2010.
[3] Gasification Technology Status- December 2010. Section 6 Ongoing RD&D of IGCC Improvements. EPRI Report # 101966. N.Holt. December 2010.

latter improvement will occur regardless of any requirement for CO_2 capture. The major energy loss components and the RD&D needed to reduce these losses are shown in Table 3-2:

Table 3-2 Pre Combustion Energy Losses and RD&D Needs

Pre-Combustion Capture Energy Loss Component	Comments/RD&D Needed	R&D in Progress	TRL of RD&D
The ASU has high auxiliary power demand for the main air compressor, oxygen and nitrogen compression	Development of ASU process with lower power demand.	Air Products ITM 1 mt/d moving to 100 mt/d oxygen	6 moving to 7
Reduction in syngas chemical heating value from the endothermic shift reaction	This loss is inevitable with the shift reaction		
Addition of steam to the shift reducing steam turbine output	Improved shift catalysts that function at a lower steam/CO ratio	All shift vendors	Various 6-8
Energy losses from cooling the shifted syngas to the temperatures required for the current AGR processes	Warm gas clean up for sulphur species and trace element removal	50 MW RTI test at Tampa	7 moving to 8
Compression energy to raise the pressure of the CO_2 recovered from AGR processes	Membranes to produce both CO_2 and Hydrogen at high pressure	Eltron test at Eastman	4 moving to 5
Limits on air extraction from gas turbines increase the auxiliary load for the main air compressor supplying air to the ASU	Gas turbine compressor designs that permit air extraction when firing hydrogen	All gas turbine vendors. DOE support of GE and Siemens. Japan for MHI.	7
Compression of the CO_2 to pipeline pressure	Produce CO_2 at higher pressure. Improved compression concepts. Improved heat recovery	RamGen	5
Reduced firing temperature of hydrogen fired gas turbines	Higher firing temperature larger gas turbines for Hydrogen provide higher efficiency and economies of scale. Need larger gasifiers to provide the hydrogen fuel for the larger gas turbines	All gas turbine vendors. DOE support for GE & Siemens. Japan for MHI	5

Potential Improvements to Supporting Technologies

ASU

The Ion Transport Membrane (ITM) for low cost oxygen production currently being developed by Air Products with major DOE support promises reduced auxiliary power usage[4]. The ceramic membrane exclusively allows only oxygen ions to migrate through the solid. The process takes place at very high temperatures of ~1,000°C (~1,832°F) and moderate pressure across the membrane is required. The current test unit is 1 mt/d and plans are moving forward for a 100 mt/d unit to be operational in 2012. The integration of this technology into IGCC or Oxy combustion plants is a significant challenge.

Shift

The shift reaction can be conducted on the sour syngas before sulphur removal ('sour shift') or after sulphur removal ('sweet shift'). Industrial catalysts are available for both types. Most IGCC + CCS designs use the sour shift approach. The major shift catalyst suppliers (SudChemie, Haldor Topsoe, and Johnson Matthey) and Shell have active programs to improve the performance of shift catalyst to operate at lower steam/CO ratios without carbon lay down or methanation issues. This is particularly important for dry coal fed gasifiers with their high CO content in the raw syngas. In an IGCC + CCS plant design based on dry fed gasifiers the steam often has to be taken from the steam cycle to meet the shift catalyst requirements thereby reducing the steam turbine output and adversely affecting the overall performance and plant efficiency.

Gas Turbines for Hydrogen

F class gas turbines have not yet been demonstrated commercially with hydrogen fuel however by reducing the firing temperature (which reduces power output and efficiency) GE, Siemens and MHI do offer F class gas turbines with commercial guarantees.

Since 2005 GE and Siemens have been developing advanced gas turbine technologies under a joint DOE sponsored initiative that is aimed at reducing syngas turbine emissions and improving efficiency of IGCC applications incorporating CCS.

The main elements of the programs are higher firing temperatures, advanced sealing and cooling, and advanced materials and coatings to allow higher temperature operation with high hydrogen content syngas. Another goal is to achieve low NOx emissions with lower use of diluent nitrogen.

Siemens has estimated that 8-9 per cent efficiency points are lost to IGCC plant designs when CO$_2$ Capture is included but that 5% efficiency can be gained back by the use of Advanced high hydrogen fired gas turbine technology. Siemens is currently offering their 8000 H gas turbines for natural gas firing and under the DOE joint program plans to adapt this design to the IGCC application.

MHI has announced plans for J type gas turbines with a firing temperature of 1600°C (100°C higher than the G turbines) and a power output about 1.2 times that of G turbines. The target availability for the J turbine on natural gas is 2011 with the first operation in 2013. The higher efficiency and greater output will provide marked improvements in IGCC economics. At the 2010 Gasification Technologies Conference, MHI outlined a future trajectory of advanced gas turbines for IGCC with the J class availability about 2017, further 1700°C gas turbines beyond 2020 and later integration with fuel cells.

The Future of Pre-Combustion Capture Technology

The next key event for the advance of pre-combustion capture technology will be the integrated operation of the first IGCC plant with capture at the Kemper County IGCC plant in Mississippi in 2014. This will hopefully be followed by some of the other IGCC projects under development.

Additional projects recovering CO$_2$ from natural gas processing (e.g. Gorgon) and possibly from natural gas reforming will also enter operation in the next few years.

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[4] Scale up and Integration of Ion Transfer Membrane Oxygen Production Technology. EPRI # 1018956

There is a very active program underway on most of the RD&D elements identified in Table 3-1 with funding from the DOE and the technology suppliers. EPRI[5] and DOE have identified a roadmap of IGCC technology developments that can potentially improve the IGCC efficiency to a level that matches or exceeds that of the current IGCC technology without capture. This is illustrated in Figure 3-3. The addition of capture with current technology reduces the efficiency by about 8 percentage points. The higher firing temperature G class gas turbines increase it by about 2.5 per cent. The use of ITM for the ASU can add another 1% to efficiency. The use of feeding the coal to the gasifier as a coal in liquid CO_2 slurry is projected to improve efficiency by about 2%. Incorporation of the RTI and Eltron advanced capture processes, together with the other advances is projected to recover the 8% efficiency loss with the current capture technologies.

With IGCC there are multiple pathways of improvements using different gasification technologies which may find particular application more favourably in certain climate conditions, locations and coal types. Figure 3-3 indicates an improvement from the use of a coal in liquid CO_2 slurry that would improve the efficiency of slurry fed gasifiers particularly for low rank coals. For dry coal fed gasifiers the development of a coal pump could produce similar efficiency gains.
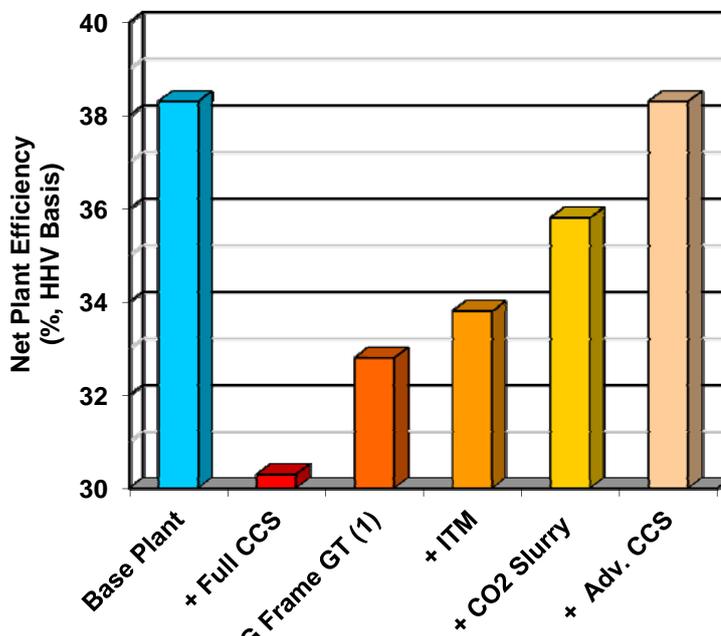

Figure 3-3 IGCC Developments to recover Energy Losses from CO₂ Capture

[5] The Future of IGCC Technology – CCPC-EPRI IGCC Roadmap Results. R. Schoff (EPRI). IEA CCT 2011. Zaragoza, Spain May 10, 2011

ACRONYMS AND SYMBOLS

AFBC	Atmospheric Fluidized Bed Combustion
AGR	Acid gas removal
AQCS	Air Quality Control System
ASU	Air Separation Unit
B&W	Babcock & Wilcox
Bara	Bars absolute
Barg	Bars gauge
BFW	Boiler feedwater
BP	British Petroleum
Btu	British thermal unit
CC	Combined Cycle
CCGT	Combined Cycle Gas Turbine
CCPI	Clean Coal Power Initiative
CCS	CO_2 capture and Storage (or Sequestration)
CCT	Clean Coal Technology
CF	Capacity Factor
CFB	Circulating fluidized bed
CHP	Combined Heat and Power
CO_2	Carbon dioxide
COE	Cost of electricity
COP	ConocoPhillips
CT	Combustion Turbine
DOE	U. S. Department of Energy
DOE NETL	Department of Energy National Energy Technology Laboratory
ECUST	East China University of Science and Technology
EEPR	European Energy Programme for Recovery
EIA	Energy Information Administration
EOR	Enhanced Oil Recovery
FBC	Fluidized-bed combustion/combustor
FEED	Front End Engineering Design
FGD	Flue gas desulphurization
FOAK	First of a kind
F-T	Fischer Tropsch
ft^3	Cubic feet
FW	Foster Wheeler
FWI	Foster Wheeler Italiana
GHG	Greenhouse Gas
GI	Gasification Island
GJ	Gigajoule
gpm	Gallons per minute (US)
GT	Gas Turbine
H_2S	Hydrogen sulfide
HgA	Mercury absolute
HHV	Higher heating value
HRSG	Heat recovery steam generator
HP	High pressure
IEA	International Energy Agency
IGCC	Integrated Gasification Combined Cycle
IP	Intermediate pressure
IPP	Independent power producer
kJ	Kilojoules
KBR	Kellogg, Brown & Root
LCA	Life Cycle Analysis
LCOE	Levelised Cost of Electricity

LHV	Lower heating value
LP	Low pressure
LSTK	Lump Sum Turnkey
mt	Metric ton
MDEA	MethylDiethanolamine
MMBtu	Million Btu
MPa	Mega Pascal
MTG	Methanol to Gasoline
MTO	Methanol to Olefins
NCCC	National Carbon Capture Center
NDRC	National Development and Reform Commission (China)
NETL	National Energy Technology Laboratory
NGCC	Natural Gas Combined Cycle
NH$_3$	Ammonia
Nm^3	Normal cubic meters
NO$_X$	Nitrogen oxides
NSPS	New Source Performance Standards
OCGT	Open Cycle Gas turbine
O&M	Operation and maintenance
PC	Pulverized Coal
PCC	Post Combustion Capture
ppmv	parts per million by volume
PRB	Powder River Basin (Coal)
PSDF	Power System Development Facility
psia	Pounds per square inch absolute
psig	Pounds per square inch gage
R&D	Research & Development
RD&D	Research, Development and Demonstration
RQ	Radiant Quench (GE)
RTI	Research Triangle Institute
RWE	Rheinische Westphalien Electricidadeswerke
SCFD	Standard Cubic Feet per day
SNG	Substitute Natural Gas
SCPC	Supercritical Pulverized Coal
SCR	Selective catalytic reduction
SO$_2$	Sulphur dioxide
SRU	Sulphur Recovery Unit
st	Short ton (2000 pounds)
stpd	Short tons per day
TCR	Total Capital Requirement
TFC	Total Field Cost
TPC	Total Plant Cost
USC	Ultra Supercritical
US EPA	US Environmental Protection Agency
WGCU	Warm gas clean up

CO$_2$ CAPTURE TECHNOLOGIES

OXY COMBUSTION WITH CO$_2$ CAPTURE
JANUARY 2012

CONTENTS

DISCLAIMER OF WARRANTIES AND LIMITATION OF LIABILITIES

OXY COMBUSTION WITH CO$_2$ CAPTURE

Oxy-combustion methods/ technologies

The nitrogen that is approximately 80% of the air commonly used for combustion serves to dilute flue gas CO$_2$ content to less than about 15% for boilers and other thermal heat recovery systems. Post-combustion capture processes are designed to separate the relatively dilute CO$_2$ from the bulk flue gas nitrogen. In oxy-combustion processes, the bulk nitrogen is removed from the air before combustion. The resulting combustion products will have CO$_2$ content up to about 90% (dry basis). If regulations and geochemistry permit, the raw, dehydrated flue gas may be stored directly without further purification. Otherwise, the flue gas impurities (predominantly O$_2$, N$_2$, and Ar) may be removed by reducing the flue gas (at moderate pressure) to a temperature at which the CO$_2$ condenses and the impurities do not.

Oxy-combustion plants will include the following major component systems.

* Air Separation Unit (ASU) – This system separates oxygen from air and supplies the oxygen for combustion.
* Combustion / Heat Transfer / Gas Quality Control system (GQCS) – The components of this system are nearly the same as components for a corresponding air-fired plant. The fuel is burned with a mixture of oxygen (from the ASU) and recycled flue gas. The combustion products are cooled to usefully recover heat and, at a minimum, cleaned of fly ash.
* CO$_2$ Purification Unit (CPU) – At a minimum, the CPU will include a flue gas drying sub-system and compressors to deliver the product CO$_2$ to a receiving pipeline or geological storage site. If required, it will also include a partial condensation process to purify the product CO$_2$ and remove impurities to specified levels.

In addition, there will be material handling systems and thermal power utilization systems, and other balance of plant systems, but these are unlikely to differ significantly from their air-fired counterparts.

Oxy-combustion may be employed with solid fuels such as coal, petroleum coke, and biomass, as well as liquid and gaseous fuels.

Oxy applications

Oxy process for power generation

In order to exploit the extensive engineering experience designing and operating air-fired combustion/heat transfer equipment, a 'synthetic air' approach is generally used for oxy-combustion processes being proposed for steam-electric power plants. In the synthetic air approach, flue gas is recycled and introduced to the combustor with oxygen in proportions that mimic the combustion and heat transfer properties of air.

The alternative approach is to employ reduced flue gas recycle (compared to the synthetic air approach) which results in higher flame temperatures. While the high flame temperature approach has been deployed with fluid fuels in selected industrial applications, there is little or no relevant commercial-scale experience with this approach in large combustion / heat transfer systems. An objective of the reduced recycle/high flame temperature approach is a commensurate reduction in combustion/heat transfer/flue gas handling capital costs.

Figure 4-1 shows a block diagram of the major component systems for an oxy-fuel steam-electric power plant.
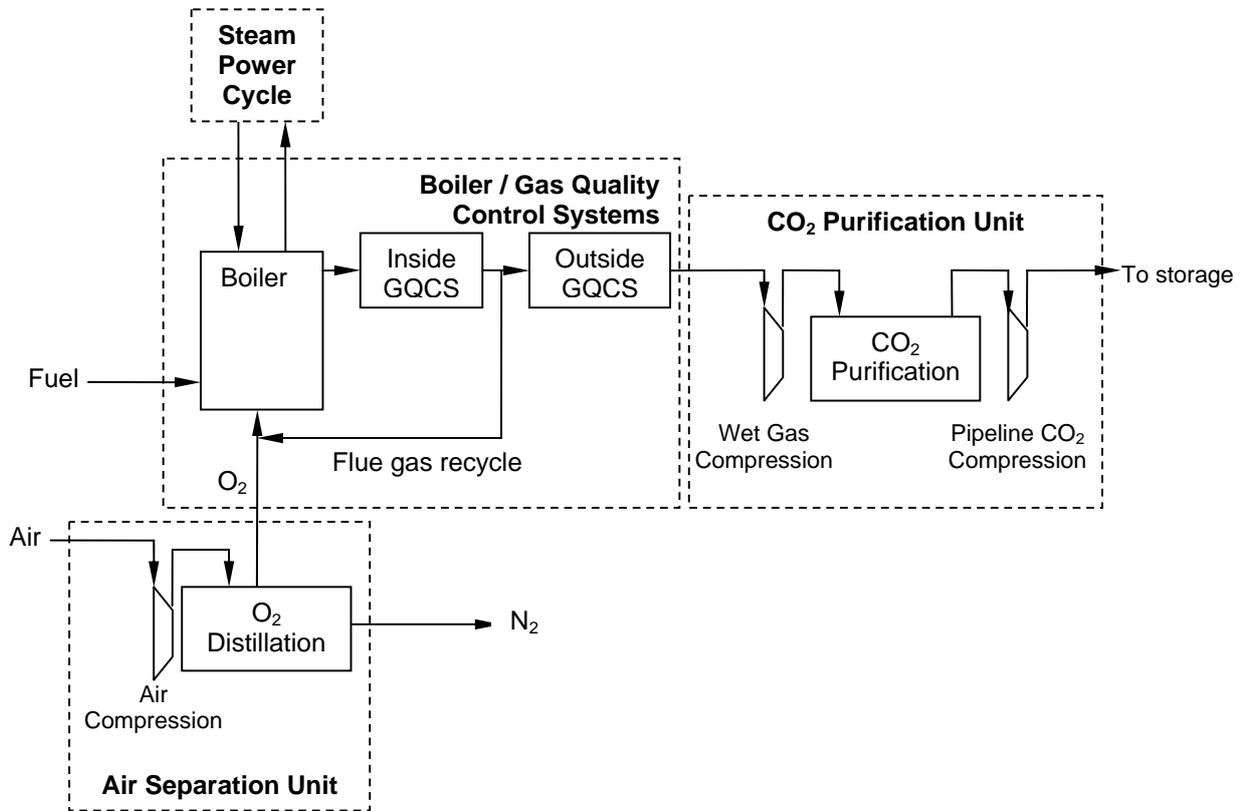
Figure 0-1: Oxy-Combustion Power Plant Simplified Block Diagram

Air separation unit

The incumbent technology for separating oxygen from air is distilling liquid oxygen at cryogenic temperatures. The technology is widely practiced on an industrial scale and is capable of producing a 99.5% pure oxygen product. It is the general industry consensus that the capital and operating cost (auxiliary power in the ASU air compressors) of producing the very high purity O_2 for oxy-combustion is not justified by the corresponding reduction in impurities in the flue gas. Thus, the O_2 produced for oxy-combustion is, typically, 95% - 97% pure, the balance being predominantly argon (Ar) and nitrogen (N_2). The primary energy cost in cryogenic air separation is auxiliary power for inlet air compression.

Combustion/heat transfer/flue gas handling systems

Boilers optimized for synthetic air oxy-combustion will be very similar to those optimized for air-combustion. Steam side temperatures and pressure capabilities developed for air-fired operation are also suitable for oxy-fired operation.

For solid fuels, either pulverized fuel or fluidized bed combustion systems may be employed. If specified, the equipment might be designed and operated to supply 100% capacity under both air- and oxy-fired conditions. Seamless transitions between air-firing and oxy-firing have been demonstrated at pilot scale.

Care must be exercised in design and construction of boiler / flue gas handling system components to minimize air in-leakage and minimize oxygen-to-flue gas leakage in recycle heaters. These leaks will serve to increase net flue gas flow rate and dilute flue gas CO_2 concentration.

Flue gas recycle

Up to 80% of the flue gas leaving the furnace is recycled to control temperatures. Net flue gas (not recycled) from oxy-combustion systems is approximately 20% - 25% that of an air-fired system due to the separation of nitrogen prior to combustion. Employing flue gas recycle will tend to increase the concentrations of minor flue gas components such as moisture, SOx, HCl, HF, and fly ash, unless means are employed to remove these materials inside the recycle loop. The same is generally true of NOx, but NOx in the recycle flow may also be destroyed in the furnace by reburning.

Flue gas quality control system costs are generally minimized by treating the net flue gas after the recycle loop rather than flue gas inside the recycle loop, due to the lower net flue gas flow. System designers are generally able to accommodate the higher flue gas moisture content without removing moisture inside the recycle loop. Fly ash is generally removed from the flue gas inside the recycle loop. The inherently lower NOx production (see below) from oxy-combustion generally does not require other active NOx removal systems.

SO$_2$ control

As in air-fired combustion, fuel sulphur is converted largely to SO$_2$ during oxy-combustion with traces of SO$_3$. SO$_2$ will accumulate in the flue gas recycle loop and, in boiler applications, must be controlled to maintain the SO$_2$ concentrations in the furnace below those at which excessive gas-side tube corrosion occurs. The accumulation of SO$_2$ in the recycle loop is illustrated in Figure 4-2 for a low-sulphur Powder River Basin (US) sub bituminous coal and a higher sulphur eastern (US) bituminous coal. The furnace SO$_2$ concentrations realized for the low sulphur fuel are sufficiently low under all conditions to not require SO$_2$ removal inside the recycle loop for boiler applications. This is not the case with the higher sulphur fuel. SO$_2$ removal from the recycle loop would be required to keep furnace concentrations below the 2,000 ppmv – 3,000 ppmv range above which gas-side tube metal corrosion would be excessive.

The SO$_2$ controls employed for air-fired flue gas are all suitable for oxy-fired flue gas. These include direct limestone injection in a circulating fluidized bed (CFB), wet flue gas desulphurization, and dry flue gas desulphurization. When forced oxidation is employed to support wet flue gas desulphurization, the oxidation vessel (where air is used to convert SO_3^{2-} to SO_4^{2-}) must be isolated from the scrubber vessel to preclude diluting the flue gas with air.
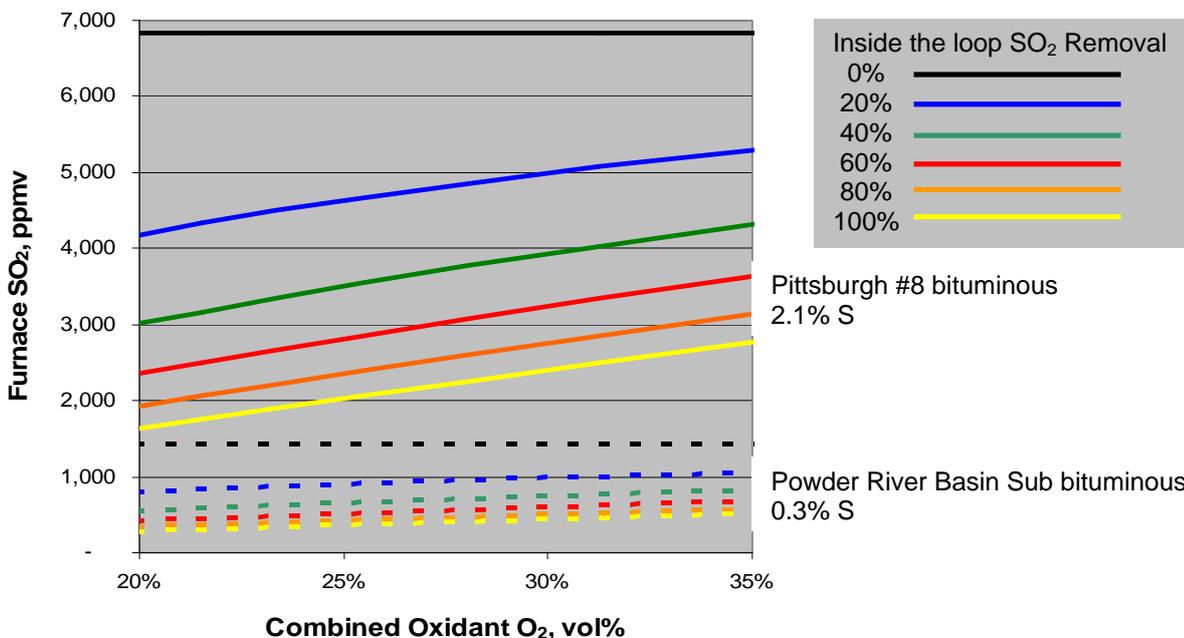

Figure 4-2: Oxy-Coal Furnace SO$_2$ content. Typical Oxy-coal process design is 25% - 30% O$_2$ in the

combined oxidant feed. Air-fired furnace SO₂ content is approximately the value at 21% O₂ and 100% Inside the Loop SO₂ Removal.

NOx control

Due to the low nitrogen concentrations at oxy-fired burners, thermal NOx production is minimized; NOx produced in the furnace comes primarily from fuel nitrogen. NOx production can be minimized by staging combustion and use of over-fire oxidant. In addition, as noted above, NOx entering the furnace with the recycle flue gas will be destroyed to a greater or lesser extent by the reburning mechanism. The aggregate effect is that, unless the facility is also specified for extended air-fired operation, the selective catalytic and selective non-catalytic NOx reduction technologies commonly employed for reducing NOx in air-fired flue gas are unlikely to be required for oxy-fired operations.

Particulate control

Removal of fly ash from oxy-fired flue gas is essentially the same as removing it from air-fired flue gas. Electrostatic precipitators or fabric filter bag houses are both suitable technologies. For designs where bag filters are cleaned by pulses of compressed gas, compressed CO_2 must be used (rather than compressed air) to preclude diluting the flue gas with air.

CO₂ purification/compression

The raw, wet flue gas entering the CPU will be cooled and compressed to intermediate pressure. CO_2 purification will always include deep drying. The dried, raw flue gas will contain 10%-30% diluents (Ar, O_2, and N_2) and trace contaminants (SO_2, SO_3, NO, NO_2, CO, etc.). If local regulations, geochemistry, and project parameters allow, the raw, dry flue gas may be compressed to pipeline or injection pressure with no further processing. Under these conditions, CO_2 capture will be 100% and there will be zero ambient air emissions.

If removal of diluents and trace contaminants is required to meet pipeline, geological or other CO_2 purity requirements, a partial condensation process is used to achieve product CO_2 purity specifications. In the partial condensation process, gases with a dew point lower than CO_2 are separated from the product CO_2 and vented. These include the diluents O_2, N_2, and Ar, the traces of CO produced in the furnace, and any residual NO not destroyed during wet compression (see below). The actual vent must be designed to effectively disperse the vent gas such that ground level concentrations of CO and CO_2 do not rise above local ambient standards. Gases with dew point higher than CO_2 (SO_2, NO_2) will condense with the product CO_2.

As indicated above, if the geochemistry, regulations, and other project parameters permit, it may be possible to compress and inject directly into storage the dried, raw flue gas. There is, however, uncertainty in the effect of the diluents and trace contaminants on the geochemistry of storing CO_2. Field experience transporting and storing dehydrated raw flue gas from oxy-natural gas combustion is being logged by Total as part of the Lacq project in southern France[1]. The CO_2 Capture Project® will be undertaking field tests for which oxy- flue gas will be stored underground[2]. Among other objectives, these activities are organized to evaluate the suitability of the impure CO_2 for geological storage.

While there are likely to be capital cost savings in not installing a CO_2 purification system, the greatest capital expense in the CPU is for compressors. There will be incrementally higher capital costs associated with larger compressors, larger pipelines, and larger storage volume to handle the diluents. Selection of pipeline materials may be affected by the diluents and trace contaminants. There may also be an incrementally higher power use associated with compressing the diluents. Various design efforts undertaken to date do not reach consistent conclusions on whether there are cost advantages to this strategy, presuming regulations and geochemistry permit[3,4,5].

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[1] Lacq *CCS Pilot Plant: Operational Feedback of the Surface Facilities One Year after Start-up.* IEAGHG 2nd Oxy-Fuel Combustion Conference. Yeppoon, Queensland, Australia. 12-16 September 2011.
[2] CO₂ Capture Project.
[3] *Energetic Evaluation of a CO₂ Purification and Compression Plant for the Oxyfuel Process.* R. Ritter, et al. IEA 1st Oxy-fuel Conference, Cottbus, Germany, September 7-10, 2009.

Cooling / Compression / Dehydration

During wet flue gas compression, much of the NOx entering with the flue gas will be oxidized to HNO_3 and captured by condensate in inter-coolers and/or final cooler/wash. The compression process may be designed to enhance NOx oxidation and capture. The compression process may also be designed to oxidize residual SO_2 to soluble SO_3 with subsequent capture along with HNO_3 in condensate.

The compressed flue gas is dried and, if a partial condensation purification process is employed, cleaned of residual mercury in the flue gas with activated carbon to preclude mercury-induced corrosion in the brazed aluminum components of the partial condensation process equipment.

The product CO_2 is finally compressed to the receiving pipeline pressure or well injection pressure. The primary energy use in the CPU is auxiliary power to perform the wet and dry compression.

Partial Condensation

Pressurized CO_2 is cooled to near -50°C (-58°F), at intermediate pressure, to condense the product CO_2. The liquid CO_2 is physically separated from the bulk impurities which are vented. Residual impurities in the liquid CO_2 may be separated by distillation to achieve a specified CO_2 purity. The liquid CO_2 is then used as a refrigerant and flashed to gaseous CO_2 to provide the refrigeration necessary for the process. The pressure drop associated with flashing the CO_2 to provide refrigeration must be made up during compression to pipeline / injection pressure.

Vent Gas CO₂ Recovery

Vent gas from a partial condensation process will largely contain the bulk impurities (O_2, N_2, and Ar) but will also contain CO_2 at a concentration up to 35%. This amounts to about 10% of the flue gas CO_2. Absorption processes and membrane processes have been proposed to recover CO_2 from the relatively modest vent gas stream at an incremental cost to capture well below the overall cost to capture CO_2. By this means, up to approximately 98% of the CO_2 in the flue gas might be captured.

Oxy-Fired Power Plant Performance

The gross power production (turbo-generator output) from an oxy-fired power plant will be essentially the same as a comparable air-fired power plant and is largely dependent on the efficiency of the steam cycle and not whether air or oxygen is used to burn the fuel. The oxy-fired plant will have increased auxiliary power use as indicated in Table 4-1. The increased auxiliary power use will serve to reduce the oxy-fired plant net power production and decrease oxy-fired plant net efficiency compared to an air-fired plant with comparable gross output. The data in Table 4-1 is 'typical' for plants employing an ultra-supercritical steam cycle with cryogenic air separation and partial condensation CO_2 purification.

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[4] *Economic Assessment of Carbon Capture and Storage Technologies*. Global CCS Institute. 2009.
[5] *Engineering and Economic Evaluation of Oxy-Fired 1100°F Ultra-Supercritical Pulverized Coal Power Plant with CO₂ Capture: Final Report*. EPRI, Palo Alto, CA: 2011. 1021782.

Table 0-1: Oxy-Coal power plant performance.

Note: An ultra-supercritical steam cycle is used. The 100% basis is the net power produced by the air-fired plant (before CO_2 capture).[6]

		Air-fired	Oxy-Fired
Gross Generation	MWe	106%	(*) 107%
ASU Power Use	MWe	-	14%
CPU Power Use	MWe	-	(**) 9%
Other Power Use	MWe	6%	7%
Net Power	MWe	**100%**	77%

(*) Increased gross generation includes thermal recovery from ASU and CPU

(**) CO_2 delivered at 150 bar, 99.99+% purity

Oxy Process for Cement Manufacture[7]

Portland cement is manufactured by calcining mixtures of limestone and silicates at temperatures in excess of 1400°C (2550°F). Fuel is burned in the calcining kilns to achieve the required temperatures. Extensive gas-solid heat recovery is practiced to minimize fuel use consistent with maintaining high product quality. Selected cement plants have employed oxygen-enriched air combustion to achieve the high kiln temperatures. Use of oxygen-enriched air allows for increased product throughput.

CO_2 emissions from the kiln include CO_2 produce by combustion of the fuel (approximately 40% of the total) and CO_2 liberated from the limestone as a result of calcining reactions (approximately 60% of the total). Flue gas CO_2 content up to 25% is experienced under these conditions. Petroleum coke is used to fire approximately half of the worldwide cement production, coal approximately a quarter, and other solid and fluid fuels the remaining quarter. Over 70% of worldwide cement manufacture capacity is located in Asia.

The overall application of oxy-combustion with CO_2 capture to cement manufacture is shown in Figure 4-3. The ASU and CPU systems are essentially the same as those described above for an oxy-combustion power boiler. The cement production process itself must be adjusted for oxy-combustion for at least two reasons: 1) the elevated CO_2 concentrations in the high temperature calcining process raises the required calcining temperature by up to 80°C (140°F), and, 2) The gas-solid heat transfer scheme which minimizes fuel use must be specifically developed for the flows and composition associated with oxy-combustion. Suitable designs for new plants can be developed, but retrofitting existing plants while maintaining production capacity and quality will be challenging. Additionally, efforts must be undertaken to minimize air in-leakage which would dilute the flue gas CO_2 content.

Particulate control is required for the flue gas being recycled and entering the CPU. As with the power boiler application, NOx production is reduced; selective and non-selective catalytic reduction systems are not required. SO_2 and SO_3 resulting from fuel sulphur combustion are captured in the cement product and no added flue gas desulphurization system is required.

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[6] Data developed from *Engineering and Economic Evaluation of Oxy-Fired 1100°F Ultra-Supercritical Pulverized Coal Power Plant with CO_2 Capture: Final Report.* EPRI, Palo Alto, CA: 2011. 1021782.
[7] *CO_2 Capture in the Cement Industry: Phase II Report.* European Cement Research Academy. TR-ECRA-106/2009. 2009.
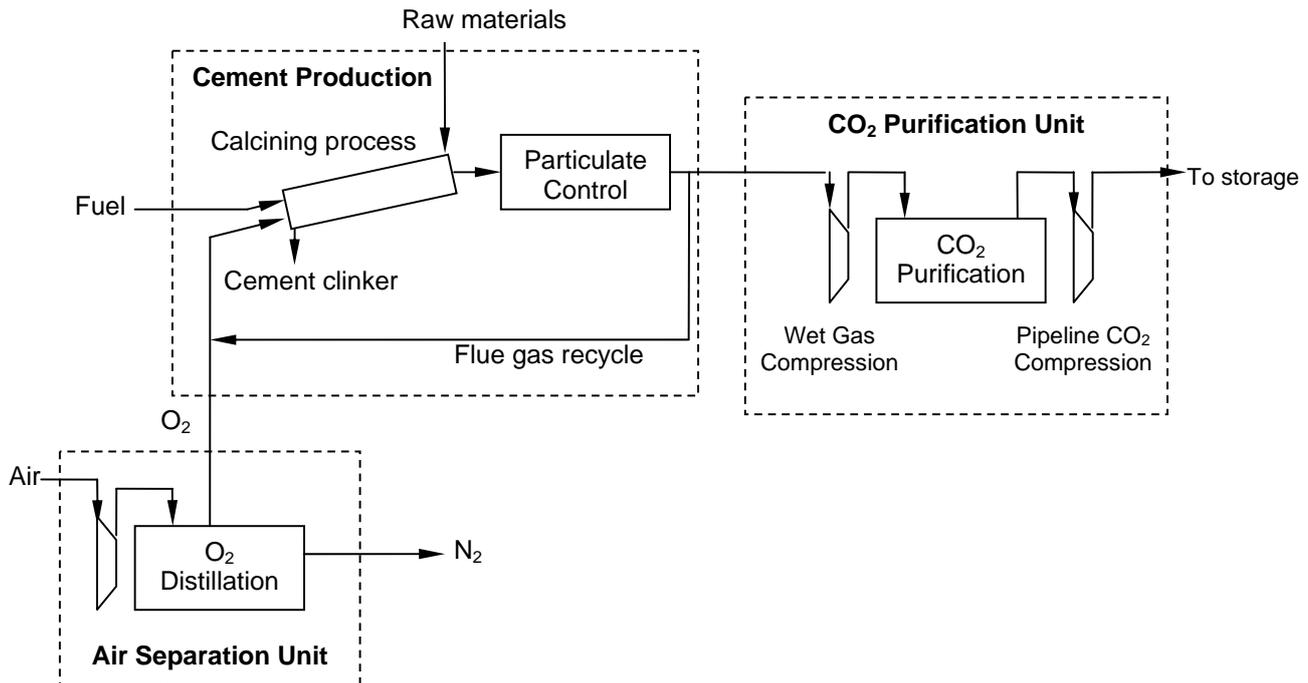
Figure 0-3: Oxy-Combustion Cement Manufacture Simplified Block Diagram

Oxy-Combustion: Current Status / Technology Providers

The component systems currently anticipated for full scale oxy-combustion applications (up to 3,200 MWth) have achieved commercial-scale readiness in other applications as follows:

- The largest single–train cryogenic ASU installed for industrial oxygen production is approximately 5,000 tonnes/day O$_2$. Three of trains of approximately this capacity would be required for a 2,000 MWth (~800 MWe) steam electric power plant. Cement plant oxygen demand will be substantially less, up to 2,000 tonnes/day. The primary design challenges for delivery of oxygen to large combustion appliances will be: 1) to optimize costs of delivering oxygen, 2) timely response to changes in oxygen demand from the host plant, and, 3) minimizing auxiliary power consistent with minimizing overall costs of delivering oxygen. Cryogenic air separation units are being offered by a number of industrial gas companies. Leading vendors include:
  - Air Products and Chemicals, Allentown, PA, USA
  - Air Liquide, Paris, France
  - Linde Engineering, Pulach, Germany
  - Praxair, Danbury, Connecticut, USA

- Under the 'synthetic' air approach, conventional, well-proven, atmospheric pressure combustion / heat transfer design tools may be used to design an oxy-fired boiler or other fired heating appliance at capacities up to 3,200 MWth heat input (~1,400 MWe). Extensive pilot-scale (<40 MWth) development of components such as burners, heat transfer surface, gas quality control systems, recycle fans, electrostatic precipitators, fabric filter bag houses, flue gas desulphurization, etc. have been undertaken by a number of vendors to validate their design tools. Leading steam-electric boiler vendors include:
  - Alstom, Levallois-Perret Cedex, France
  - Babcock and Wilcox, Barberton, Ohio, USA
  - Foster-Wheeler, Clinton, New Jersey, USA
  - Doosan Babcock, Crawley, West Sussex, United Kingdom

- Babcock-Hitachi, Tokyo, Japan
- Mitsubishi Heavy Industries, Tokyo, Japan

- Partial condensation CO$_2$ purification units are in service at industrial scale, removing a wide variety of contaminants depending on the source of the CO$_2$. None of these installations have all of the impurities commonly found in coal-fired flue gas. Neither do any of these facilities employ the auto-refrigeration process (using the liquid CO$_2$ produced as the refrigerant) envisioned for large oxy-combustion plants. The largest single-train partial condensation CO$_2$ purification process deployed commercially is approximately 4,000 tons CO$_2$ per day. Four trains of approximately this capacity would be required for a 2,000 MWth plant (~800 MWe) power plant.

  - Air Products and Chemicals, Allentown, PA, USA
  - Air Liquide, Paris, France
  - Linde Engineering, Pulach, Germany
  - Praxair, Danbury, Connecticut, USA

The greatest remaining technical challenge is integrating these systems into a complete steam-electric power plant.

It should be noted that the oxy-combustion/CO$_2$ capture power plant designs being developed and deployed for service in the next 4-5 years are based on individual component technologies and arrangements which have demonstrated sufficient maturity. These plant designs, however, may not be optimized. As experience is gained, it is likely that evolutionary changes in oxy-combustion plant flow sheets (with CO$_2$ capture) will serve to reduce capital and operating costs and improve plant performance.

Pilot Plant Projects Underway

Vattenfall has operated a dried lignite-fueled 30 MWth pilot plant at their Schwartze Pumpe power station in Germany since mid-2009[8]. Component systems installed include ASU, oxy-PC boiler, gas quality control systems, and externally-cooled, partial condensation CPU. Liquid CO$_2$ is trucked off-site to industrial markets.

The Schwarze Pumpe project has shown achievement of TRL-6 for oxy-combustion with CO$_2$ capture (for application to electric power production). The results of the project have given Vattenfall sufficient confidence in the technology to progress to design of a 250 MWe oxy-coal sub-scale commercial demonstration plant.

Total's Lacq project, located west of Lyon, France, has also shown achievement of TRL-6 for oxy-natural gas combustion and geological storage of raw, dried oxy-combustion flue gas. Component systems include an ASU, an oxy-natural gas 30 MWth boiler, flue gas cleaning/compression/drying and direct injection of the raw, dried flue gas into a depleted natural gas reservoir[9]. This plant has been in service since early 2010.

CIUDEN is completing construction of an oxy-coal test facility in Spain that includes a 20 MWth oxy-PC boiler and a 30 MWth oxy-CFB boiler. Liquid oxygen is trucked to the site. A slip stream CPU is employed. Oxy-coal operations will commence in 2011. Successful operations at CIUDEN will show achievement of TRL-6 for oxy-combustion with CO$_2$ capture as applied to electric power production

CS Energy has converted a retired 100 MWth (25 MWe) pulverized coal power plant to oxy-combustion at the Callide station in Queensland, Australia. The facility includes an ASU, oxy-PC boiler, steam turbo-generator, and a slip stream CPU capturing approximately 10% of the CO$_2$ produced. The liquid CO$_2$ will be trucked to storage site injection wells. Oxy-coal operations will commence in 2011. Successful operation of this plant will show achievement of TRL-7 for oxy-combustion with CO$_2$ capture as applied to electric power production.

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[8] *Oxy-Combustion Testing in 30 MWth Pilot Plant Schwartze Pumpe.* IEAGHG 2nd Oxy-Fuel Combustion Conference. Yeppoon, Queensland, Australia. 12-16 September 2011.
[9] Lacq *CCS Pilot Plant: Operational Feedback of the Surface Facilities One Year after Start-up.* IEAGHG 2nd Oxy-Fuel Combustion Conference. Yeppoon, Queensland, Australia. 12-16 September 2011.

Sub-Scale Commercial Demonstration Plants in Development

Four sub-scale commercial demonstration plants are in development world-wide. All of these are in the planning/engineering stages and the decision to proceed to construction has yet to be made. These projects will result in a commercially-dispatched, integrated, oxy-coal steam electric power plants. Successful operation of one or more of these plants would show achievement of TRL-8 for oxy-combustion with CO_2 capture as applied to electric power production.

Full Scale Commercial Projects in Development

There are currently no full scale (1,000 – 2,000 MWth) oxy-fired projects under development.

Technical Readiness of Oxy-Combustion for Cement Manufacture

The European Cement Research Academy (ECRA) has developed a research and development plan that would result in a demonstration plant (successful operation of which would achieve TRL-8 or TRL-9) project starting in the 2014-2015 time frame[10]. Preliminary studies undertaken by ECRA have achieved TRL-5[11]. Laboratory and Process Development unit activities are underway to achieve TRL-6 in 2011. The plan calls for construction and operation of an oxy-combustion cement manufacture pilot plant, successful operation of which would achieve TRL-7, in the 2011-2014 time frame.

Oxy Future Direction / Challenges

Retrofit / Repowering

Existing air-fired power plants might be retrofitted with an ASU, oxy-fired burners, flue gas recycle, and a CPU. The resulting plant would be derated by the auxiliary power these systems consume less any improvement in steam cycle capacity that might be available. Alternatively, the existing plant, typically a sub-critical steam cycle, might be repowered by adding an ultra-supercritical topping steam cycle and a new, ultra-supercritical, oxy-fired boiler. While such retrofit/repowering schemes have been proposed, it has yet to be shown that they can result in an oxy-fired plant that is lower in cost than an optimized, new-build plant. The large fleet of air-fired power plants in service, however, calls for more study of this option.

Lower-cost O_2 production

The cryogenic ASU is costly and the largest auxiliary power use in an oxy-fired power plant is for the air compressors in the ASU. Any oxygen separation process that reduces auxiliary power is likely to be an economic boon to the oxy-combustion option. Two of the leading technologies under investigation:

- Chemical Looping Combustion (CLC) – oxygen is separated from nitrogen by a reversible reaction with suitable solids which are then transferred to a 'combustor' where the solid-oxygen reaction is reversed, the fuel burned, and the resulting CO_2 produced in concentrated gas stream. Bench-scale activities are on-going to identify suitable solids (work to achieve TRL-5). Process development units are being constructed for developing solids handling schemes and to characterize performance of the candidate solids and the overall process[12] (work to achieve TRL-6). A successful CLC process would dramatically reduce auxiliary power use in air separation by replacing the air compressors in a cryogenic ASU with fluidizing blowers in the CLC process.

- Ion Transport Membrane (ITM) – Selected ceramic materials exclusively allow oxygen ions to migrate through the solid. The process takes place at very high temperatures (~1,000°C, ~1,800°F) and moderate pressure across the membrane is required. Operations are underway to achieve TRL-7 with the native ITM

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[10] *CO₂ Capture in the Cement Industry: Phase II Report.* European Cement Research Academy. TR-ECRA-106/2009. 2009.

[11] *ibid.*

[12] *Chemical Looping Combustion Prototype – Alstom.* National Energy Technology Center, US Department of Energy. Contract Number: DE-NT0005286. May 2011.

technology[13]. In addition to developing the native ITM technology, it will be a challenge to effectively integrate the native technology into an oxy-combustion power plant.

Low Recycle Operations

Reducing the flue gas recycle required for 'synthetic air' has the potential to reduce boiler size/cost. Low-recycle operations a have been conducted at PDU scale (~15 MWth) achieving TRL-6.

Pressurized Oxy-Coal Combustion

Conducting the oxy-combustion under gas pressure would marginally reduce auxiliary power, primarily in the flue gas recycle fan. A gas-pressurized boiler plant could also reduce latent heat loses in the flue gas (higher boiler efficiency) by recovering the heat of flue gas moisture condensation at a temperature usable to the power cycle. Pressurized oxy-combustion process development has been conducted at the 5 MWth level, achieving TRL-6. There are a number of developers proposing pressurized oxy-combustion pilot plant operations which would achieve TRL-7 but none of these have reached the deployment stage. There is relevant pressurized air-coal combustion experience up to 250 MWth which might be applicable.

A parallel challenge to pressurized oxy-combustion process development is development of the associated gas-pressurized boiler design. Capital costs for pressurized oxy-coal power plants with uncertainty comparable to atmospheric pressure oxy-coal power plants await more detailed component designs, particularly the gas-pressurized boiler.

Ultra-low Emissions

By its nature, an oxy-coal power plant is likely to be a 'near zero' emitter of all criteria pollutants excepting, possibly, carbon monoxide. This is a side effect of either: 1) compressing and storing the entire flue gas flow (zero emissions to the ambient air), or, 2) the nature of the partial condensation CO_2 purification process. Carbon monoxide production is comparable to air-firing, and, if a partial condensation purification process is employed, the CO will be vented along with the bulk flue gas impurities (including oxygen). Provisions for oxidizing the vent gas CO would reduce steady state emissions of all criteria pollutants to 'near zero'.

In addition, suitable start-up and shut-down sequences of operation which do not require air-firing (and resultant elevated NOx production) might be developed and for which near-zero emissions levels would be achieved for all operating states.

GQCS – CPU optimization

The unique chemistry of NOx and SO_2 during wet compression might be exploited to reduce or eliminate bulk flue gas desulphurization requirements in the flue gas quality control system, transferring bulk desulphurization to the CPU. This would potentially result in a significant overall plant capital cost reduction.

Prospective Oxy-Combustion Power Plant Efficiency Improvements

The state of the art (2011) in steam-electric power plant design employs a high efficiency, ultra-supercritical steam turbine cycle. Such a cycle would likely be selected for an oxy-fired power plant with CO_2 capture employing an atmospheric pressure boiler. An analysis has been conducted on the performance and cost of such a power plant in comparison to an air-fired power plant employing the same steam turbine-generator[14]. The air-fired plant has a net power generating efficiency of 39.0% (HHV). The comparable oxy-fired plant has a net efficiency of 31.5%, a 7.5 percentage point drop associated with power used in the ASU air compressors and CPU CO_2 compressors, and flue gas recycle fan.

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[13] *Development of Ion Transport Membrane (ITM) Oxygen Technology for Integration in IGCC and Other Advanced Power Generation System.* National Energy Technology Center, US Department of Energy. FT40343, June 2011.
[14] *Engineering and Economic Evaluation of Oxy-Fired 1100°F Ultra-Supercritical Pulverized Coal Power Plant with CO_2 Capture: Final Report.* EPRI, Palo Alto, CA: 2011. 1021782

The several future efficiency improvements to the oxy-combustion process for power generation include:

- employing an Advanced USC steam turbine cycle: 680C/700C/352 bar (1256F/1292F/5100psia), approximately 3.5 percentage point improvement;
- gas pressurised oxy-combustion – reduction of recycle fan auxiliary power use and improvement of boiler efficiency, approximately 1.4 percentage point improvement; and
- chemical looping combustion for O$_2$ separation – dramatic reduction of auxiliary power used in air separation, approximately 5 percentage point improvement.

These data are shown in Figure 4-4. The benefits of both gas pressurized oxy-combustion and chemical looping combustion may be difficult to achieve together. Nonetheless, chemical looping combustion combined with an advanced ultra-supercritical steam turbine cycle may well be more than adequate to make up for the added auxiliary power in the CO$_2$ purification unit and recycle fan resulting in an oxy-combustion plant with near zero emissions of conventional pollutants, up to 98% CO$_2$ capture, and efficiency comparable to the best power plants currently being built.
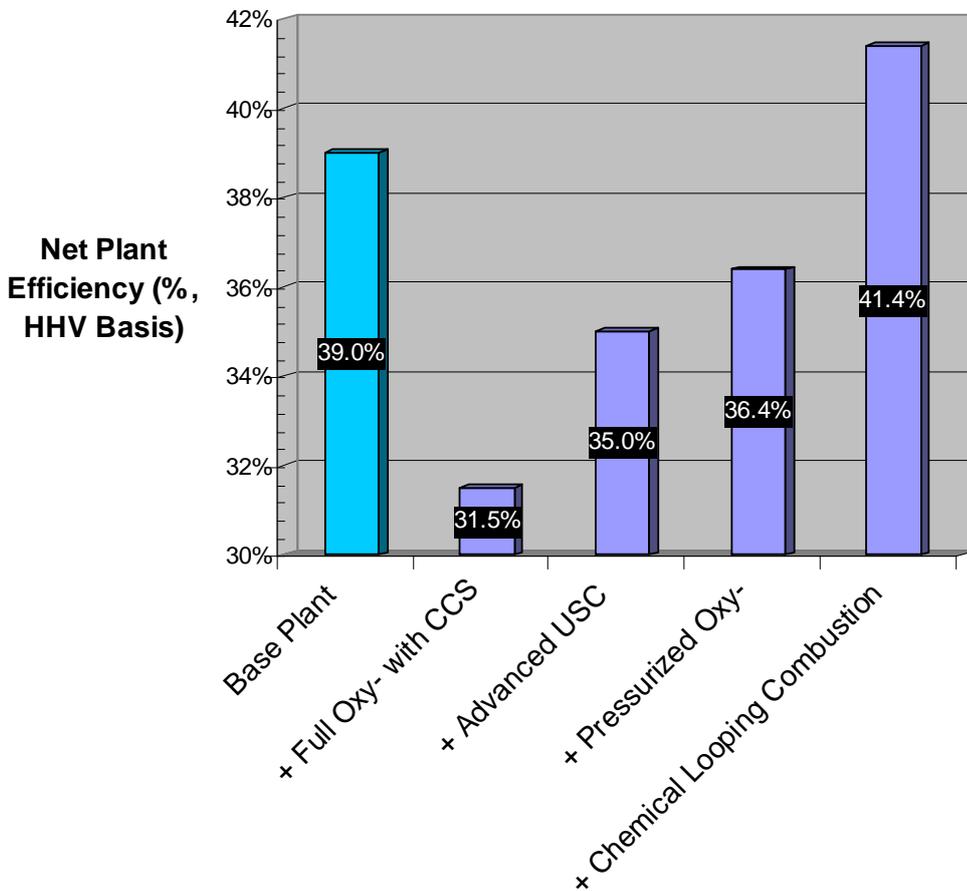

Figure 0-4: Oxy-Combustion Developments to recover Energy Losses from CO$_2$ Capture
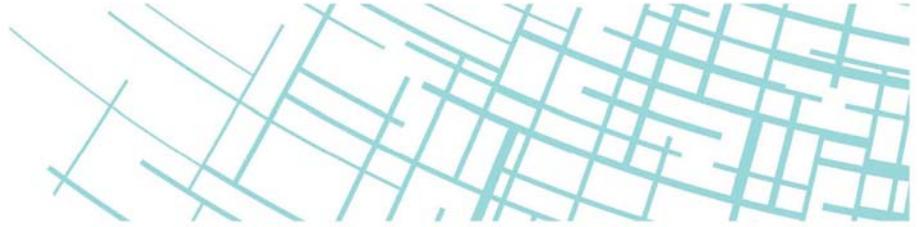
ACRONYMS AND SYMBOLS

AFBC	Atmospheric Fluidized Bed Combustion
AGR	Acid gas removal
AQCS	Air Quality Control System
ASU	Air Separation Unit
B&W	Babcock & Wilcox
Bara	Bars absolute
Barg	Bars gauge
BFW	Boiler feedwater
BP	British Petroleum
Btu	British thermal unit
CC	Combined Cycle
CCGT	Combined Cycle Gas Turbine
CCPI	Clean Coal Power Initiative
CCS	CO$_2$ capture and Storage (or Sequestration)
CCT	Clean Coal Technology
CF	Capacity Factor
CFB	Circulating fluidized bed
CHP	Combined Heat and Power
CO$_2$	Carbon dioxide
COE	Cost of electricity
COP	ConocoPhillips
CT	Combustion Turbine
DOE	U. S. Department of Energy
DOE NETL	Department of Energy National Energy Technology Laboratory
ECUST	East China University of Science and Technology
EEPR	European Energy Programme for Recovery
EIA	Energy Information Administration
EOR	Enhanced Oil Recovery
FBC	Fluidized-bed combustion/combustor
FEED	Front End Engineering Design
FGD	Flue gas desulphurization
FOAK	First of a kind
F-T	Fischer Tropsch
ft^3	Cubic feet
FW	Foster Wheeler
FWI	Foster Wheeler Italiana
GHG	Greenhouse Gas
GI	Gasification Island
GJ	Gigajoule
gpm	Gallons per minute (US)
GT	Gas Turbine
H$_2$S	Hydrogen sulphide
HgA	Mercury absolute
HHV	Higher heating value
HRSG	Heat recovery steam generator
HP	High pressure
IEA	International Energy Agency
IGCC	Integrated Gasification Combined Cycle
IP	Intermediate pressure
IPP	Independent power producer
kJ	Kilojoules
KBR	Kellogg, Brown & Root
LCA	Life Cycle Analysis
LCOE	Levelised Cost of Electricity

LHV	Lower heating value
LP	Low pressure
LSTK	Lump Sum Turnkey
mt	Metric ton
MDEA	MethylDiethanolamine
MMBtu	Million Btu
MPa	Mega Pascal
MTG	Methanol to Gasoline
MTO	Methanol to Olefins
NCCC	National Carbon Capture Center
NDRC	National Development and Reform Commission (China)
NETL	National Energy Technology Laboratory
NGCC	Natural Gas Combined Cycle
NH$_3$	Ammonia
Nm^3	Normal cubic meters
NO$_X$	Nitrogen oxides
NSPS	New Source Performance Standards
OCGT	Open Cycle Gas turbine
O&M	Operation and maintenance
PC	Pulverized Coal
PCC	Post Combustion Capture
ppmv	parts per million by volume
PRB	Powder River Basin (Coal)
PSDF	Power System Development Facility
psia	Pounds per square inch absolute
psig	Pounds per square inch gage
R&D	Research & Development
RD&D	Research, Development and Demonstration
RQ	Radiant Quench (GE)
RTI	Research Triangle Institute
RWE	Rheinische Westphalien Electricidadeswerke
SCFD	Standard Cubic Feet per day
SNG	Substitute Natural Gas
SCPC	Supercritical Pulverized Coal
SCR	Selective catalytic reduction
SO$_2$	Sulphur dioxide
SRU	Sulphur Recovery Unit
st	Short ton (2000 pounds)
stpd	Short tons per day
TCR	Total Capital Requirement
TFC	Total Field Cost
TPC	Total Plant Cost
USC	Ultra Supercritical
US EPA	US Environmental Protection Agency
WGCU	Warm gas clean up

CO₂ CAPTURE TECHNOLOGIES

POST COMBUSTION CAPTURE (PCC)

JANUARY 2012

CONTENTS

This document has been derived from material in the report sponsored by the Global Carbon Capture and Storage Institute, Canberra, Australia. *CO$_2$ Capture Technologies July 2011.*

POST COMBUSTION CAPTURE (PCC)

Basic Descriptions of Post-Combustion Capture

Post-combustion capture (PCC) refers to the separation of CO$_2$ from flue gas derived from combusting fossil fuels – coal, natural gas, or oil – in air. In the case of coal-based power, as shown in Figure 1-1, coal is combusted in air and the liberated heat is converted to electricity by steam-driven turbines connected to generators. The combustion results in a flue gas mixture consisting of N$_2$, CO$_2$, H$_2$O, O$_2$, and a host of compounds such as SO$_x$, NO$_x$, and heavy metals amongst others. Some of these are removed using existing technologies such as selective catalytic reduction (SCR), electrostatic precipitation (ESP), and flue-gas desulphurization (FGD). A PCC process then aims to selectively separate CO$_2$ from the remaining gas mixture as shown in Figure 2-1. After capture, CO$_2$ can be compressed and stored underground, used in some other processes such as enhanced oil recovery (EOR), or used in some other capacity that does not result in its emission into the atmosphere.
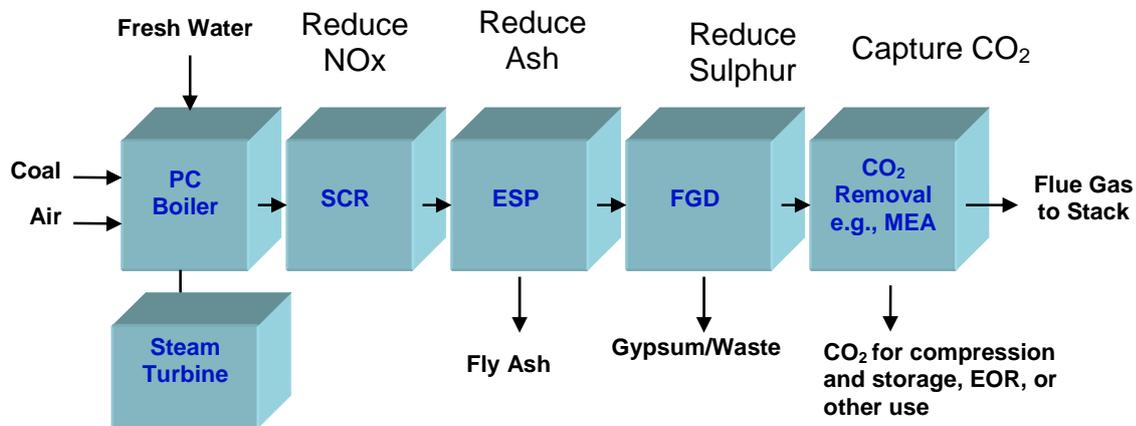
Figure 2-1. A Typical Post-Combustion Carbon Capture Process.

Influence of Fuel

Table 2-1 shows the representative concentration of post-combustion flue gas for coal- and gas-fired power plants. There is additional variation around these values depending on the exact composition of the fuel, the efficiency of the plant, types of emission controls installed, and other factors, but for purposes of CO$_2$ capture, 10-15% CO$_2$ for coal and 4-5% for natural gas are quite representative.

Table 2-1 Typical Compositions of Flue gases from Coal- and Gas-fired Power Plants.

Gas Constituent	Coal	Natural Gas (Gas Turbine)
Nitrogen (N$_2$)	70-75%	73-76%
Carbon Dioxide (CO$_2$)	10-15%	4-5%
Water Vapour (H$_2$O)	8-15%	8-10%
Oxygen (O$_2$)	3-4%	12-15%
Trace Gases (SO$_x$, NO$_x$, others)	<1%	<1%

Carbon is the predominant combustion species in coal, while both carbon and hydrogen are combusted in natural gas; thus, for each CO$_2$ molecule generated during combustion, coal has less energy release. This results in coal power plants typically generating twice as much CO$_2$ as gas power plants for the same power output, about 1 g CO$_2$/kWh vs. 0.5 g CO$_2$/kWh. However, flue gas from coal power plants has more concentrated CO$_2$ relative to natural gas. This results in CO$_2$ capture consuming less energy for coal power plants relative to gas power plants for the same mass of CO$_2$ captured. The net result in terms of parasitic load on the host power plant and cost of electricity increase due to the capture process therefore is not straight forward particularly with the range of coal and natural gas prices. Due to the predominance of coal in power production and the likelihood of CO$_2$-control regulations impacting those most, the overwhelming emphasis of capture process developers has been on coal-fired power plants. Research and development for capture on natural gas fired power plants is relatively scarce, though regulations may require natural gas fired power plants to have CO$_2$ emission controls similar to that expected for coal fired power plants.

Near-Term Technologies

PCC technologies that can be considered near-term have been tested at scales on slip streams no larger than 5-25 MWe from coal-fired power plants. Press releases and other announcements have been made for projects intended for larger sizes, but these are planned future projects. All near-term technologies are solvent-based involving either ammonia or proprietary amines. The distinction between these technologies is specific capture chemistry and, to some extent, the process configuration and integration into the power plant. The specific capture chemistry can be contaminated by the presence of other acid-forming gases such as SO$_2$ and SO$_3$, and therefore all of these near-term technologies require SO$_x$ concentrations typically no higher than 10 ppmv in order to minimize solvent usage and cost

Technologies that could be called near-term include Fluor's Econamine FG+, Mitsubishi Heavy Industries KS solvent, Cansolv Technologies, Aker Clean Carbon, and Alstom's Chilled Ammonia Process (ACAP). All of these use either aqueous pure amines or blends of amines, with the exception of Alstom's CAP which uses aqueous ammonium carbonate to bicarbonate reaction. In all these near-term technologies, an absorber-stripper configuration is used as shown in Figure 2-1, with the solvent regenerated thermally using steam from the power plant. This steam extraction results in loss of power production at the host plant, and when combined with power needed for compression, results in a parasitic load of 20-30% for CO$_2$ capture and compression, with net plant efficiency dropping from 38% to 27%. Hence, most near-term technologies seek to not only improve capture chemistry, but also seek to use sources of waste thermal energy at the power plant and the compression train to assist in solvent regeneration.

It should also be noted that emissions from amine-based capture processes are still being studied. Initial reports from testing in Norway indicated that possible reaction products may exit the absorber either as volatile gases or mechanically entrained droplets, including nitrosamines. Research in understanding of such emissions is active, and a number of groups are attempting to understand the risk of such emissions, the potential impact of such emissions on health and the environment if any, and possible strategies to minimize emissions.

The following notes provide a technical status report[1] on each of the post combustion capture technologies that have been selected for large scale demonstration.

Fluor Econamine FG Plus^{SM} and Other MEA Processes

For over thirty years, amine scrubbing with monoethanolamine (MEA) in aqueous solution has been used to capture CO_2 from the flue gas of fossil-fuelled boilers and petrochemical process heaters. The first significant large-scale CO_2 capture plant in the United States, at the Searles Valley Minerals Plant in Trona, California, has remained in continuous operation since 1978 with two parallel trains each capturing 400 ton/day (363 mt/day) of CO_2 from flue gas from a coal-fired boiler. The CO_2 is used to carbonate brine for soda ash manufacture. The ABB Lummus Global Process, using a 15–20% by weight MEA solution with inhibitors, has also been used for CO_2 capture with slipstreams from three smaller coal-fired power boilers. The process, however, is still relatively small compared to full scale power plants. A typical 500 MWe coal-fired power plant, for instance, generates about 12,500 mt CO_2/day, and about 11,300 mt CO_2/day would have to be captured to yield a 90% capture rate.

Fluor's Econamine FG Plus^{SM} technology is said to reduce steam consumption by over 30% compared to 'generic' MEA technology. Econamine FG Plus adds a number of refinements to the Econamine FG^{SM} solvent and process, which have been used in 25+ commercial plants for the recovery of CO_2 from flue gas at rates from 6 to 1000 mt/day. The flue gas processed was mainly produced by combustion of natural gas; four units use flue gas from natural gas steam reformers. Although none of the units process coal-derived flue gas, the latest Econamine FG Plus formulation is targeted at that market.

Proprietary inhibitors, to control corrosion, oxidative degradation, and thermal degradation allow use of MEA at higher concentration (30–35%+ by weight solution versus 18–20% previously) to more efficiently recover CO_2 from low-pressure streams containing oxygen at concentrations of 1–15% by volume. The Econamine FG Plus formulation has an increased CO_2 absorption rate, allowing use of a smaller absorber and lower reboiler steam flow, and has reduced makeup requirements. The Econamine FG Plus process uses absorber intercooling and a split flow configuration to help reduce energy requirements. Fluor has also developed advanced solvent reclamation technologies and heat integration strategies such as flue gas-heated reboilers. Econamine FG Plus is a candidate technology for several PC-CCS demonstrations in the United States, Canada, and Europe.

Because of the prevalence of its predecessor technology in flue-gas applications, Econamine FG Plus is often used as a representative technology for economic evaluation of PC technologies without and with CCS (and for comparison to IGCC without and with CCS).

MHI KM-CDR Process

Another near-term technology for coal-fired power plants is MHI's KM-CDR process that uses the KS-1 sterically hindered amine solvent developed by MHI and Kansai Electric Power Company. A 25 MWe equivalent capture and storage demonstration (100–150,000 tonnes-CO_2/year) is scheduled to begin operation this year at Alabama Power's, James M. Barry Electric Generating Plant. Construction has been initiated and start up is planned for the second half of 2011. This project is fully coordinated with storage of 500 mt/d of the captured CO_2 in the Citronelle formation as part of the DOE's SECARB regional sequestration partnership program.

Demonstrations using KM-CDR are also planned in Europe and Australia. KM-CDR is a refined version of a process that has been in commercial use since 1990 with oil- and gas-based flue gas at up to 450 mt/day scale. In 2006, MHI and J-Power began a 10 mt/day pilot test with coal-based flue gas at Matsushima power station in southern Japan. KS-1 claims significantly better CO_2 loading and stripping energy requirements than MEA solvents, and lower volatility, compared to MEA, which reduces solvent makeup requirements. Unit cost of the solvent is higher by a factor of about five. The KS-1 solvent also requires low levels of SOx and NOx

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[1] Holt, N., Dillon, D., Marasigan, J., and Hendrix, H. *Coal Technologies with CO₂ Capture – Status, Risks, and Markets 2010*; PID 1019658; EPRI, Palo Alto, CA, 2010

(typically 1ppm) and therefore requires upstream polishing of flue gas to achieve these absorber input requirements. MHI claims that KM-CDR circulation rate is 60% of that for (unspecified) MEA, regeneration energy is 68% of MEA, and solvent loss and degradation are 10% of MEA. MHI is working on process improvements that are said to have potential to reduce the regeneration heat requirement to 800 Btu/lb-CO$_2$ (1860 kJ/kg) from ~1200 Btu/lb-CO$_2$ (2790 kJ/kg).

Alstom Chilled Ammonia Process (ACAP)

Alstom's Chilled Ammonia Process is a more recent technology that was developed to address specific concerns regarding post-combustion capture of CO$_2$ from coal-fired power plants. Following a 1.7 MWe pilot at We Energies Pleasant Prairie Power Plant in Wisconsin, a nominal 20 MWe equivalent, 100,000 ton-CO$_2$/yr capture and storage pilot began operation in September 2009 at AEP's Mountaineer Power Plant and to date about 25,000 mt has been captured at typically 80-90% capture efficiency and at 99.9+ % purity. The project also includes CO$_2$ injection that was initiated in October 2009 and through May 2011, over 50,000 mt had been captured of which 37,000 mt had been injected.

Announced plans include a 20 MW equivalent application at Statoil Hydro's Mongstad Test Center in Norway (from a NGCC plant and refinery cracker slipstream). The 235 MW, 1.5 million ton-CO$_2$/yr demonstration at AEP's Mountaineer plant in West Virginia was selected for funding under the DOE CCPI 3 initiative but is not proceeding for lack of legislative and financial incentive.

ACAP uses the changes in chemical equilibrium of ammonia, ammonium carbonate, and ammonium bicarbonate with change in temperature to capture and release CO$_2$ from the flue gas stream. ACAP has an advantage in its use of a low-cost solvent that resists degradation with elevated temperature and with exposure to SO$_X$ and NO$_X$. Use of a higher stripping temperature also allows ACAP to release CO$_2$ at a higher pressure than is possible with the amine solvents. However, ACAP requires a larger absorber because it has a relatively low reaction rate and CO$_2$ loading, and loses some efficiency to the chiller, which is required to maintain reaction temperature.

Powerspan ECO$_2$™ Process

PowerSpan's ECO$_2$™ process has been reformulated to use a proprietary solvent incorporating a mixture of aqueous amines. ECO$_2$ no longer requires use of PowerSpan's ECO or ECO-SO$_2$ process, as had been stated for the prior ammonia/ammonium carbonate formulation. Validation testing in a 1 MWe equivalent (~ 20 stpd) pilot at FirstEnergy's R. E. Burger Plant ran from December 2008 into 2010. In May 2010, Powerspan announced that an independent assessment had concluded that the technology is ready for scale-up, with a cost of less than $40 per ton of CO$_2$ captured and compressed, based on a 220 MWe net retrofit project size. Process improvements during testing were said to reduce the regeneration steam requirement to less than 1000 Btu/ lb-CO$_2$ (2326 kJ/kg).

Cansolv

Cansolv, a former subsidiary of Union Carbide now owned by Shell Global Solutions International B.V., has developed aqueous diamine regenerable solvents for the selective or sequential removal of SO$_2$, NO$_X$ with mercury, and CO$_2$. Reported CO$_2$ capture rates of 90% have been achieved on a 150 m^3/hr (85 ACFM) lignite flue gas slipstream. Startup is planned for early 2011 for a modularized system capturing 50 mt/day of CO$_2$ from a slipstream at RWE npower's Aberthaw PC plant in Wales. The retrofit of a 150 MWe unit at SaskPower's Boundary Dam will use Cansolv DS to achieve 100% SO$_2$ capture upstream of the Cansolv DC103 CO$_2$ capture system. The Cansolv SO$_2$ capture system produces saleable H$_2$SO$_4$ by-product, instead of a solid waste requiring disposal, and produces heat that can be used to provide part of the CO$_2$ solvent regeneration energy. In April 2011 the Saskatchewan Government approved the Boundary Dam project. Key equipment had been pre-ordered to enable a planned start up in 2014. The refurbished 150 MW unit will produce 115 MW net power after retrofit. The Boundary Dam units are all fired with Saskatchewan lignite.

Aker Clean Carbon

Aker Clean Carbon's Just Catch technology has been refined through slipstream testing on PC plant flue gas with a portable pilot unit installed at Scottish Power's Longannet station. In November 2009, Scottish Power announced that testing of process improvements and low-energy solvents had achieved a reduction in energy requirement of about one-third compared to a reference plant. Reduced solvent emissions are a claimed benefit of the Just Catch process.

Aker has built a mobile amine pilot facility which is completing its testing at the National Carbon Capture Center in Wilsonville, Alabama, using coal-derived flue gas. The unit will be transported to the Statoil Hydro's Technology Centre Mongstad and expected to start up there in December 2011. (The pilot is also connected to the nearby refinery cracker.) The pilot will be 40 MWth equivalent, capturing up to 25,000 mt/yr with NGCC-CHP flue gas containing 3.5% CO_2. With refinery process flue gas containing 12.9% CO_2 (similar to flue gas from a PC plant) the capture rate would be up to 73,000 mt/yr.

Alstom Advanced Amine Process

Alstom and Dow Chemical Company are working jointly on process refinement with a pilot facility using proprietary Dow amine solvent (DOW UCARSOL^{TM} FGC 3000) on flue gas from a coal-fired boiler at a Dow chemical plant in South Charleston, West Virginia. Alstom will build and operate a second R&D facility at the EDF Group's Le Havre (France) thermal energy plant, with start-up by 2012. This facility would be used to test and refine the Alstom Advanced Amine process using coal-derived flue gas. Subsequent demonstrations are proposed for the 858 MW SCPC lignite-fired unit now under construction at the Elektownia Belchatow plant in Poland. A 20 MW$_{th}$ pilot would be followed by a 250 MWe, 1.8M mt/yr CCS demonstration, with a targeted 2015 start-up. The Dow amine is claimed to capture CO_2 with increased efficiency, higher tolerance for oxygen and trace contaminants, and decreased solvent degradation.

Siemens POSTCAP Amino Acid Salt

Siemens Energy and TNO, the Netherlands Organization for Applied Scientific Research, have begun working together to advance their separately developed, second-generation amino acid salt processes. In comparison to amines, the amino acid salt technology is said to absorb CO_2 rapidly with a high CO_2 loading and lower solvent flow rate, resist oxidation, have reduced heat of regeneration, have lower volatility, and be environmentally benign. Siemens studies indicate that use of POSTCAP with CO_2 compression to 200 bar (2900 psi) would reduce the net efficiency of a 600°C (1112°F) USCPC plant from 45.7% LHV to 35.9% LHV and would not increase plant water consumption.

In August 2009, Siemens began operation of a 1 MWe equivalent pilot unit at E.ON's Staudinger 5 PC unit near Hanau, Germany. In September 2010, DOE announced an additional Industrial Carbon Capture award, allowing Siemens to increase the size of a planned POSTCAP pilot, on a PC plant slipstream, from 1 MWe to 2.5 MWe equivalent. The pilot at Tampa Electric Company's Big Bend Power Station in Ruskin, Florida, has a 2013 start-up target.

Siemens is performing a CCS study for the 695 MWe-net advanced SCPC Longview Power Generation Facility project, for which Siemens provided environmental control equipment. The Longview plant is now under construction in Maidsville, West Virginia, with a 2011 start-up target.

HTC Purenergy / Doosan Babcock

Doosan Babcock Energy has partnered with HTC Purenergy to commercialize a mixed amine solvent process that was initially developed at the University of Regina, Saskatchewan, and field tested in a pilot unit operated by the University of Regina International Test Center at SaskPower's Boundary Dam coal plant, near Estevan, Saskatchewan. HTC Purenergy claims that pilot testing and process optimization has reduced regeneration energy to less than 1.0 ton steam per ton CO_2 (about 30% less than conventional 30% MEA). Doosan Babcock will be performing further development at a newly commissioned RD&D pilot in Renfrew, Scotland.

HTC has performed a FEED study for a 450 MW NGCC plant and developed a modularized, pre-assembled design for a 1,000 mt/day capture system that is scalable to 3,000 mt/day. Basin Electric Power Cooperative

(BEPC) contracted Doosan Babcock Energy to perform a FEED study for 120 MWe equivalent post-combustion CO_2 capture demonstration at the 450 MW Antelope Station. This project had previously been selected for funding support under the DOE CCPI-3 program however after being unable to secure a contract for the CO_2, Basin Electric decided in December 2010 not to proceed with the project.

Other Solvent Processes

Around the world, several other technologies are among those at the maturity level that makes them candidates for near-term demonstrations at small commercial scale.

- In early 2010, ENEL commissioned a 2.5 tons/hr slipstream capture pilot at Brindisi (Italy) Unit 4, using an advanced amine (MEA) process developed by IFP (Institute France Petrol). Liquefied CO_2 is to be stored on site, used in a flow test loop, and trucked offsite for geologic sequestration. A 2015 start-up is targeted for a full-stream capture unit on a new 660 MWe unit at Porto Tolle with saline aquifer storage.

- The Korea Electric Power Research Institute's of KoSol 1 and KoSol 2 advanced amine solvents at 5 MW equivalent scale is planned to continue through 2015.

- A TPRI amine process is capturing CO_2 for industrial uses at 100,000 tonne/year scale at the Shidongkou 2 power plant in Shanghai, China.

- In Australia CSIRO have three PCC pilot projects at Loy Yang in Victoria, Delta's Munmorah plant in New South Wales and with Tarong in Queensland. The Loy Yang project (CO_2 ~1000 mt/y) was started up in 2008. The Munmorah project (CO_2 ~3000 mt/y) started up in February 2009.

Major Challenges and R&D Trends

The major challenges in PCC revolve around the relatively large parasitic load CCS imposes on a power plant, the majority of which is due to capture, especially the energy needed to regenerate the solvent. Energy required for compression, though important, is less than that required for capture and is closer to its thermodynamic limit than capture is to its thermodynamic limit. Hence, development of new chemistry, new process designs, and novel power plant integration schemes all aimed at reducing the parasitic load of CCS are the focus of virtually R&D in PCC. In general, capital cost reductions, solvent degradation, solvent volatility, and other such parameters are secondary to the prime issue of reduction in parasitic load on the host power plant imposed by the PCC process itself. These secondary issues, while important, do not constitute the major challenge in PCC, and much of the R&D trend is focusing on the reduction in parasitic load of PCC processes. These trends are discussed next, grouped according to the capture method employed.

Capture Methods

Virtually all capture processes use an absorbent (solvent), adsorbent (solid sorbent), and membranes, with far lesser emphasis on converting CO_2 to a mineral, employing biofixation, or other beneficial use of CO_2.[2,3,4,5]

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[2] Freeman, B. and Rhudy, R. *Assessment of CO₂ Capture Options Currently Under Development;* PID 1012796; EPRI, Palo Alto, CA, 2007.

[3] Bhown, A.S., Freeman, B. *Program on Technology Innovation: Post-Combustion CO₂ Capture Technology Development;* PID 1016995; EPRI, Palo Alto, CA, 2008.

[4] Bhown, A.S., Freeman, B. *Post-Combustion CO₂ Capture Technology Development;* PID 1017644; EPRI, Palo Alto, CA, 2009.

[5] Bhown, A.S., Freeman, B. *Post-Combustion CO₂ Capture Technology Development;* 1019812 EPRI, Palo Alto, CA, 2010.

Absorption

Absorption refers to the uptake of CO$_2$ into the *bulk phase* of another material – for example, dissolving CO$_2$ molecules into a liquid solution such as an aqueous amine. Absorption is used widely in the chemical, petrochemical, and other industries, and as a result, operational confidence in absorption process is high. Indeed, virtually all near-term and mid-term PCC processes under development are absorption based. In a solvent-based PCC process (see Figure 2-2), flue gas is contacted with the solvent which typically contains a reagent that selectively reacts with CO$_2$. This contact occurs in traditional gas-liquid contactors, and CO$_2$ transfers from the gas phase into the liquid phase. The CO$_2$-loaded rich solution is pumped to a regenerator vessel where it is heated to liberate gaseous CO$_2$ and the lean solution is circulated back to the absorber. The liberated gaseous CO$_2$ is collected, dried, compressed and transported to a storage reservoir, or it may be used in some other application such as EOR.
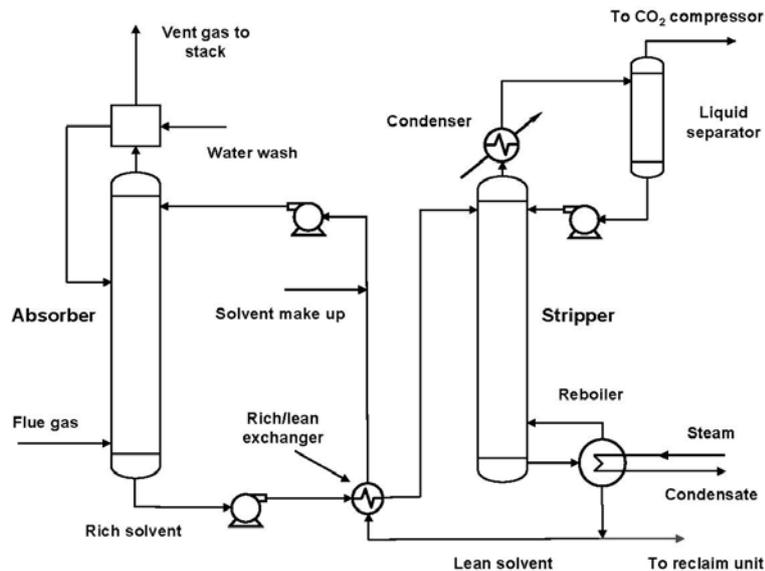

Figure 2-2. Absorption-based PCC process

The most common example of a PCC absorption process is 30 wt% aqueous monoethanolamine (MEA) which has been used commercially capturing up to 1000 tonne/day of CO$_2$. Current estimates of capture with MEA followed by compression for underground storage impose approximately 30% parasitic load on the net output of a power plant and increase the cost of electricity by 60-90%. These relatively high values result from the relatively large quantity of energy needed to regenerate the solvent. Therefore, much of the current research in absorption-based PCC is focus on development of new solvents that reduce the regeneration energy. Examples of such new chemistries include Alstom's Chilled Ammonia Process which uses a reaction of ammonium carbonate to ammonium bicarbonate as well as a host of proprietary amines from Mitsubishi Heavy Industries, Cansolv, Aker, PowerSpan's ECO$_2$^{TM}, amongst as number of other process developers. Some early-stage research is also being conducted in more novel chemistries involving ionic liquids, phase separation solvents, and siloxane oligomers.

Adsorption

Adsorption refers to uptake of CO$_2$ molecules onto the *surface* another material – for example, adhering CO$_2$ molecules onto the surfaces of a solid sorbent such as 13X zeolites. A claimed advantage of adsorption is that the regeneration energy should be lower relative to solvents since the heat capacity of the solid sorbent is lower than aqueous solvents. However, such claims based on singular rationale are often insufficient, and a careful analysis requires consideration of multiple effects such as heat capacity, working capacity, and heats of reaction. These analyses are not straightforward, do not often point to one clear technology choice over another, and is the subject of early-stage research to help guide development of new capture materials. Potential disadvantages for adsorbents include particle attrition, handling of large volumes of sorbent and thermal management of large-scale adsorber vessels.

As shown in Figure 2-3a, adsorption typically occurs via weak Van der Waals forces for physisorption or stronger covalent bonding for chemisorption. Adsorption processes are implemented most often with the adsorbent used in packed beds or fluidized beds. In a packed bed (See Figure 2-3b), adsorbent is loaded into a column, flue gas flows through the void spaces between the adsorbent particles, and the CO_2 adsorbs onto the particle surfaces. In fluidized beds (See Figure 2-3c), flue gas flows upward through a column at velocities such that the adsorbent particles are suspended in the gas flow. Regardless of the process configuration, the adsorbent selectively adsorbs CO_2 from the flue gas, and is subsequently regenerated by lowering the pressure and/or increasing the temperature to liberate the adsorbed CO_2. In a packed bed configuration, regeneration is accomplished by heating the CO_2-laden adsorbent to liberate CO_2. During this time, flue gas is diverted to a second packed bed which continues to adsorb CO_2 from the gas. By alternating flue gas between two packed beds that alternatively undergo absorption and regeneration in a cycle, CO_2 can be continually removed from flue gas. In a fluidized bed, the sorbent is circulated between an absorber vessel where it contacts flue gas and a regenerator vessel where it is heated to liberate gaseous CO_2.
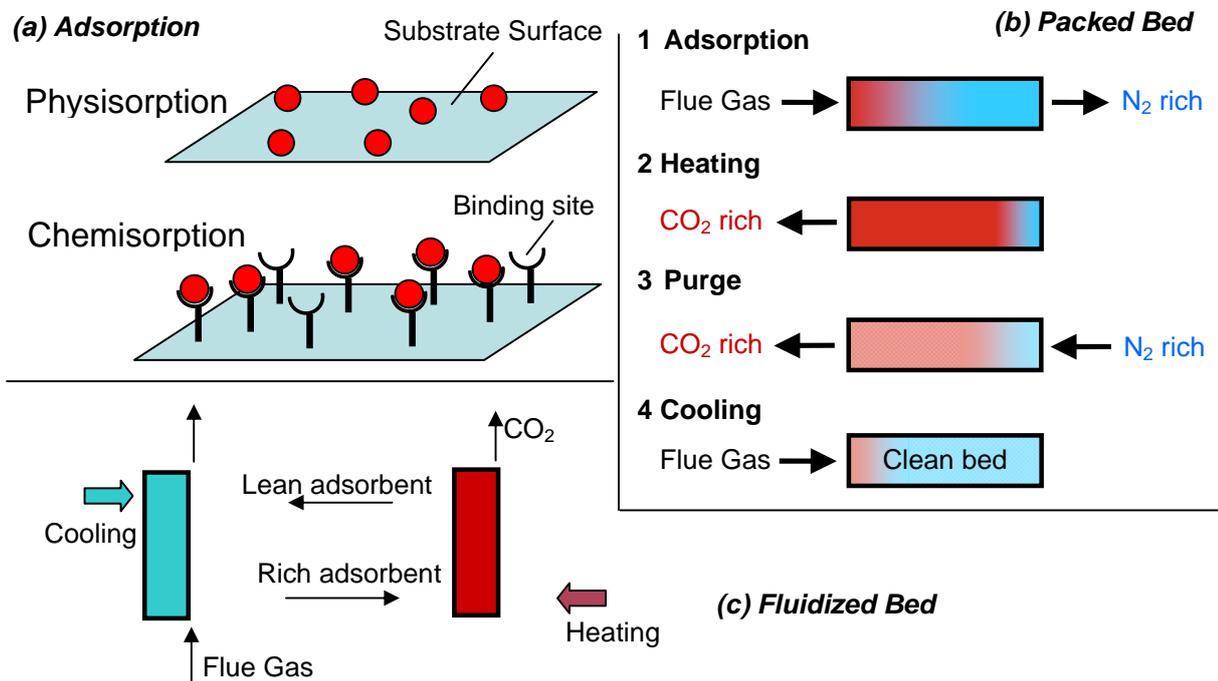

Figure 2-3. Adsorption-based PCC process.

Adsorption processes for PCC are still in the kW range of demonstration; examples include ADA-ES which is conducting a screening effort to identify suitable capture materials for scale-up, as well as CO_2CRC and Monash University which are jointly conducting research in materials and process development for pressure-swing adsorption. Earlier stage work is focused on development of entirely new materials such as metal organic frameworks (MOFs), zeolites and zeolitic imidazolate frameworks (ZIFs) at mostly academic institutions.

Membranes

Membranes can separate CO_2 from flue gas by selectively permeating it through the membrane material. If CO_2 has a higher permeability (permeability, defined as the product of solubility and diffusivity, in the membrane relative to other species in the flue gas, then CO_2 will selectively permeate the membrane. In some cases, chemical agents that selectively react with CO_2 are also added to the membrane to increase the membrane's selectivity for CO_2. CO_2 transports a membrane only if its partial pressure is higher on one side of the membrane relative to the other side. This partial pressure gradient can be obtained by pressurizing the flue gas on one side of the membrane, applying a vacuum on the other side of the membrane, or both, as shown in

Figure 2-4. Depending on the selectivity of the membrane, multiple membrane stages may be needed in order to obtain sufficiently high CO_2 purity.

Like adsorbents, membranes are claimed to potentially offer low energy capture processes. Additional benefits could include a small foot-print for the capture system and a modular design that may allow for flexible operation. However, little data exists on membrane systems for PCC, and testing has been conducted at scales less than 1 mt/day with results that are not yet publicly available. The major challenge for membranes comes from the potential fouling of the membrane surfaces from particulate matter, uncertainty about the performance and cost of large-scale efficient vacuum pumps and compressors required for PCC, and the ability to integrate the process into a power plant. Some of these issues are still being resolved at the laboratory and bench-scale with 1 MWe scale testing planned in 2012-2013 time frame.
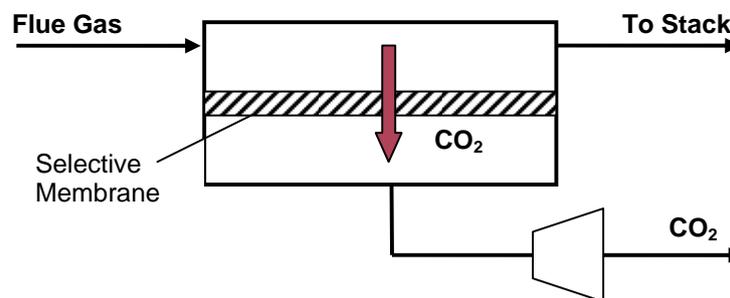

Figure 2-4. A Membrane-based PCC process.

Membrane processes are in general less widely used for separations, and therefore as a class, are also further from commercialization in PCC as well. Membrane Technology and Research (MTR) has proposed a novel process configuration along with novel membrane materials that could reduce the parasitic load on a power plant. In MTR's process, flue gas and air flow across the two surfaces of CO_2-selective membrane, and the CO_2 permeates from the flue gas into the air. The CO_2-enriched air is then sent to the boiler for combustion. This effectively forms a loop that enriches the CO_2 from 13% to approximately 18% in flue gas. A second CO_2-selective membrane unit then removes CO_2 by applying a vacuum. The process has been tested at 1 tonne CO_2/day scale and is currently being scaled to 20 tonnes CO_2/day at a coal-fired power plant. However, such integration into the power plant has not yet been tested with membrane processes. Other developments around membranes for PCC are still in the laboratory stages, focusing chiefly on improving the membrane material properties.

Current Status

The exclusive emphasis is currently on absorption on near-term technologies, reflecting the fact that industry's CO_2 capture chemistry knowledge and overall process experience are both heavily slated towards absorption.

As mentioned previously the parasitic loss of net power from the use of the MEA solvent technology is about 30% so that the major focus of R&D in PCC is on processes and equipment that can reduce this energy loss.

EPRI has undertaken an extensive look at the landscape of CO_2 capture technologies, including evaluating some 120 PCC technologies on a Technology Readiness Level ranking.[2,3,4,5] Most of these could be assigned a TRL ranking, while some could not because they are extremely early-stage concepts and do not yet have a process per se. Figure 2-5 shows a histogram of the TRL ranking for 95 of the 120 technologies studied.
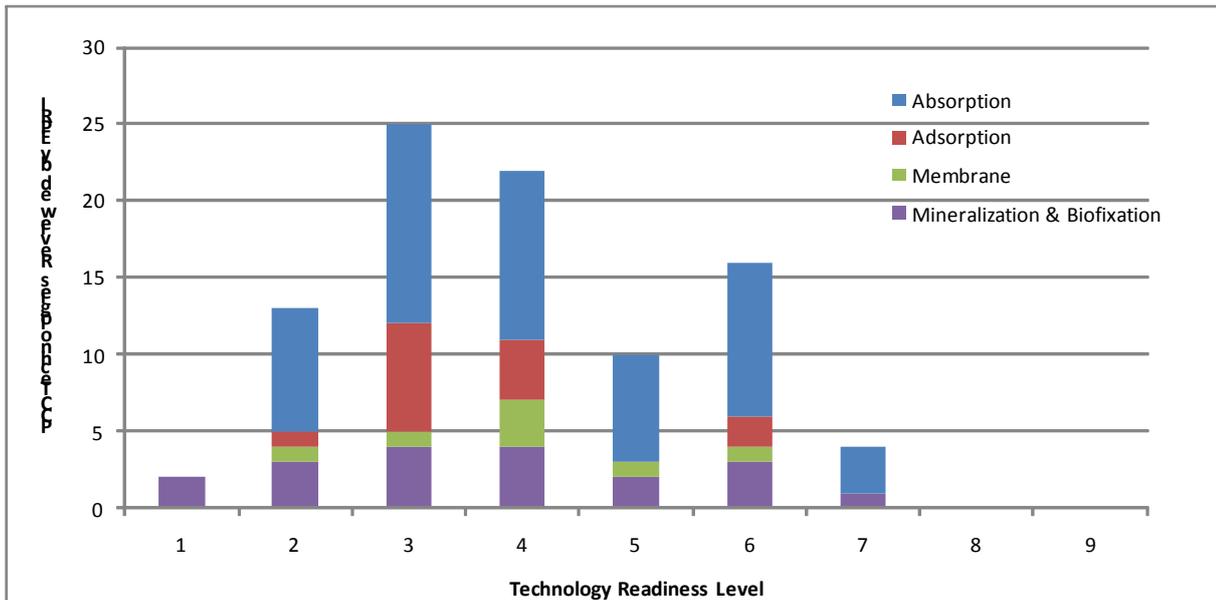
Figure 0-5 PCC **Technology Readiness Level Ranking**

Most technologies are focused on absorption with adsorption and membranes less so. As described earlier, absorption dominates the near-term, higher TRL technologies. However, these near-term technologies also will tend to be ones with higher parasitic load on the power plants. Further-term technologies, reflected at lower TRL rankings, potentially do offer PCC technologies with lower parasitic loads on power plants, but these are further from development.

Table 2-2 shows an overall status of the major types of PCC technologies. The usage of the technology in the chemical process industry and operational confidence are obviously correlated. As discussed above, major reason for energy consumption by the capture process for absorption is thermal regeneration of the solvent; for adsorbent-based processes its thermal and/or vacuum regeneration; and for membranes, it's either pressurizing the flue gas and/or applying vacuum to the permeate-side. Development trends universally are across decreasing the energy consumption of the PCC process by focusing on new capture chemistry, novel capture process development, regeneration at pressure and better thermal integration into the power plant.

Table 2-2 State of Post-Combustion CO$_2$ Capture Development

	Absorbent	**Adsorbent**	**Membrane**
Commercial Usage in CPI*	High	Moderate	Low/Niche
Operational Confidence	High	High, but complex	Low to moderate
Primary Source of Energy Penalty	Solvent Regeneration (thermal)	Sorbent Regeneration (thermal/vacuum)	Compression on feed and/or vacuum on permeate
Development Trends	New chemistry, thermal integration	New chemistry, process configuration	New membrane, process configuration

* Chemical Process Industries

The Future of Post-Combustion Capture Technology

While post-combustion capture is perhaps the most widely studied, the 20-30% parasitic load imposed by the process is deemed to be high. As a result, a multitude of approaches are being attempted that are currently at various stages of development. The near-term technologies are universally aqueous based solvents, and as such, they represent the higher-parasitic load processes. The further-term technologies may potentially impose lower-parasitic loads, but there is considerable uncertainty in their projections.

Figure 2-6 shows the potential for PCC technologies for a new build 595°C power plant using Powder River Basin (PRB) coal with various regeneration energies of an aqueous amine solvent.[6] The final column shows that increasing the boiler temperature to 705^{0}C with an advanced amine solvent increases the net plant efficiency by about 2% on a higher heating value basis. Changing from PRB coal to bituminous coal, which has higher heat content, will add another 2% to all the values in the graph.

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[6] Dillon, D., Chu, R., Choi, G., Harper, W., Sugita, S. *An Engineering and Economic Assessment of Post-Combustion CO$_2$ Capture for 1100°F Ultra-Supercritical pulverized Coal Power Plant Application;* PID 1017515; EPRI, Palo Alto, CA 2010.
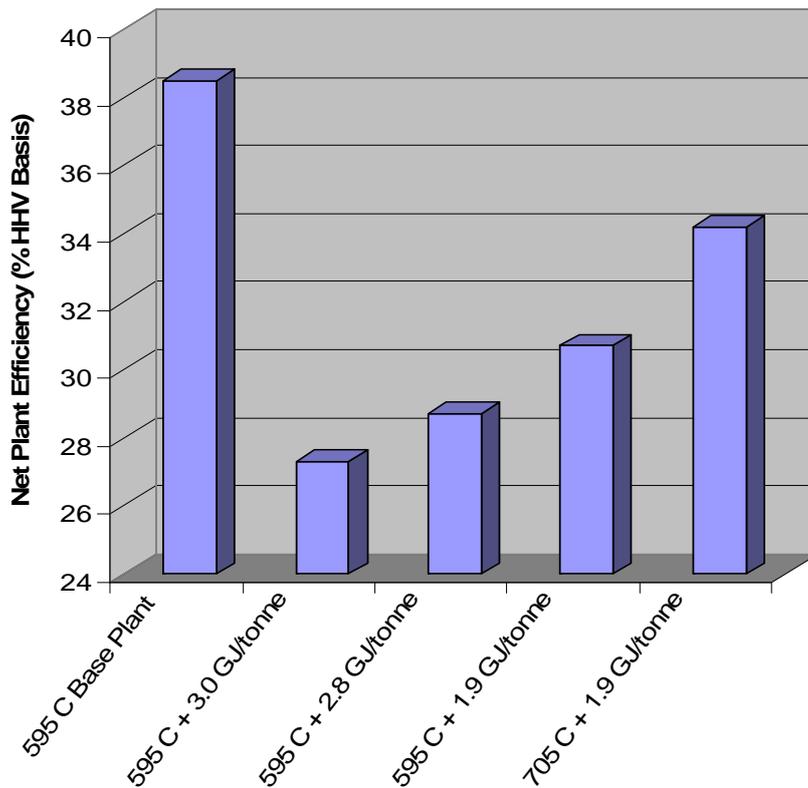
Figure 2-6. Projected performance of PCC technologies with near-term aqueous amine solvents.

A final and critical point is that in the EPRI analysis, the current landscape of CO$_2$ capture technology development involves three groups working largely independent of each other: chemists who design and synthesize appropriate separation materials, process engineers who can design separation processes around those materials, and power plant engineers who can integrate the process into a power plant. The emergence of breakthrough technologies will require close interdisciplinary collaboration between these groups which need to have an understanding of how their work mutually depends on the other.

ACRONYMS AND SYMBOLS

AFBC	Atmospheric Fluidized Bed Combustion
AGR	Acid gas removal
AQCS	Air Quality Control System
ASU	Air Separation Unit
B&W	Babcock & Wilcox
Bara	Bars absolute
Barg	Bars gauge
BFW	Boiler feedwater
BP	British Petroleum
Btu	British thermal unit
CC	Combined Cycle
CCGT	Combined Cycle Gas Turbine
CCPI	Clean Coal Power Initiative
CCS	CO_2 capture and Storage (or Sequestration)
CCT	Clean Coal Technology
CF	Capacity Factor
CFB	Circulating fluidized bed
CHP	Combined Heat and Power
CO_2	Carbon dioxide
COE	Cost of electricity
COP	ConocoPhillips
CT	Combustion Turbine
DOE	U. S. Department of Energy
DOE NETL	Department of Energy National Energy Technology Laboratory
ECUST	East China University of Science and Technology
EEPR	European Energy Programme for Recovery
EIA	Energy Information Administration
EOR	Enhanced Oil Recovery
FBC	Fluidized-bed combustion/combustor
FEED	Front End Engineering Design
FGD	Flue gas desulphurization
FOAK	First of a kind
F-T	Fischer Tropsch
ft^3	Cubic feet
FW	Foster Wheeler
FWI	Foster Wheeler Italiana
GHG	Greenhouse Gas
GI	Gasification Island
GJ	Gigajoule
gpm	Gallons per minute (US)
GT	Gas Turbine
H_2S	Hydrogen sulfide
HgA	Mercury absolute
HHV	Higher heating value
HRSG	Heat recovery steam generator
HP	High pressure
IEA	International Energy Agency
IGCC	Integrated Gasification Combined Cycle
IP	Intermediate pressure
IPP	Independent power producer
kJ	Kilojoules
KBR	Kellogg, Brown & Root

LCA	Life Cycle Analysis
LCOE	Levelized Cost of Electricity
LHV	Lower heating value
LP	Low pressure
LSTK	Lump Sum Turnkey
mt	Metric ton
MDEA	MethylDiethanolamine
MMBtu	Million Btu
MPa	Mega Pascal
MTG	Methanol to Gasoline
MTO	Methanol to Olefins
NCCC	National Carbon Capture Center
NDRC	National Development and Reform Commission (China)
NETL	National Energy Technology Laboratory
NGCC	Natural Gas Combined Cycle
NH_3	Ammonia
Nm^3	Normal cubic meters
NO_X	Nitrogen oxides
NSPS	New Source Performance Standards
OCGT	Open Cycle Gas turbine
O&M	Operation and maintenance
PC	Pulverized Coal
PCC	Post Combustion Capture
ppmv	parts per million by volume
PRB	Powder River Basin (Coal)
PSDF	Power System Development Facility
psia	Pounds per square inch absolute
psig	Pounds per square inch gage
R&D	Research & Development
RD&D	Research, Development and Demonstration
RQ	Radiant Quench (GE)
RTI	Research Triangle Institute
RWE	Rheinische Westphalien Electricidadeswerke
SCFD	Standard Cubic Feet per day
SNG	Substitute Natural Gas
SCPC	Supercritical Pulverized Coal
SCR	Selective catalytic reduction
SO_2	Sulphur dioxide
SRU	Sulphur Recovery Unit
st	Short ton (2000 pounds)
stpd	Short tons per day
TCR	Total Capital Requirement
TFC	Total Field Cost
TPC	Total Plant Cost
USC	Ultra Supercritical
US EPA	US Environmental Protection Agency
WGCU	Warm gas clean up