
Coal-fired CCS demonstration plants, 2012

Stephen Mills

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Abstract

The present report reviews activities taking place focused on the eventual large-scale deployment of carbon capture systems on coal-fired power plants. With this aim in mind, there are three main CO₂ capture technology streams currently being developed and tested; these comprise pre-combustion capture, post-combustion capture, and systems based on oxyfuel technology. Although numerous other capture systems have been proposed, these three are currently the focus of most RD&D efforts and this report concentrates on these. More speculative technologies still at early stages in their development are not addressed.

The overall aims of this report are to provide an update of recent technological developments in each of the main categories of CO₂ capture, and to review the current state of development of each, primarily through an examination of larger-scale development activities taking place or proposed. However, where appropriate, data generated by smaller-scale testing is noted, especially where this is feeding directly into ongoing programmes aimed at developing further, or scaling-up the particular technology. Each is reviewed and the status of individual coal-based projects and proposals described. These are limited mainly to what are generally described as pilot and/or demonstration scale. Where available, learning experiences and operational data being generated by these projects is noted. Technology Readiness Levels (TRLs) of individual projects have been used to provide an indication of technology scale and maturity.

For pre-combustion capture, post-combustion capture and oxyfuel systems, an attempt has been made to identify the technological challenges and gaps in the knowledge that remain, and to determine what technology developers are doing in terms of RD&D to address these. However, issues of commercial confidentiality have meant that in some cases, information in the public domain is limited, hence it has only been possible to identify overarching aspirational goals, rather than to report on individual detailed research plans and proposals.

Acronyms and abbreviations

AAP	advanced amine process
A/E	architect/engineer
AGR	acid gas removal
aMDEA	activated methyldiethanolamine
ASU	air separation unit
BOP	balance of plant
CAP	chilled ammonia process
CAPEX	capital expenditure
CCC	Clean Coal Centre
CCGT	combined cycle gas turbine
CCS	carbon capture and storage
CCT	clean coal technology
CFBC	circulating fluidised bed combustion
CFD	computational fluid dynamics
CIUDEN	Fundación Ciudad de la Energía
CO	carbon monoxide
CO ₂	carbon dioxide
CSLF	Carbon Sequestration Leadership Forum
CTL	coal-to-liquids
DEA	diethanolamine
DIPA	di-isopropylamine
EEPR	European Energy Programme for Recovery
EOR	enhanced oil recovery
EPC	engineering, procurement and construction
EPRI	Electric Power Research Institute
ESP	electrostatic precipitator
FEED	front end engineering and design
FF	fabric filter
FGD	flue gas desulphurisation
FT	Fischer-Tropsch
GCCSI	Global Carbon Capture and Storage Institute
GQCS	gas quality control system
HAZOP	hazard and operability
IEA	International Energy Agency
IEA GHG	International Energy Agency Greenhouse Gas R&D Programme
IGCC	integrated gasification combined cycle
ITM	ion transfer membrane
LHV	lower heating value
LSIP	large-scale integrated project
MDEA	methyl diethanolamine
MEA	monoethanolamine
MHI	Mitsubishi Heavy Industries
MCR	maximum continuous rating
MVA	monitoring, verification, and accounting
NETL	National Energy Technology Laboratory
NZEP	near-zero emissions plant
OECD	Organisation for Economic Co-operation and Development
OPEX	operating expenditure
OTM	oxygen transfer membrane
PSA	pressure swing adsorption

PCC	pulverised coal combustion
PRB	Powder River Basin
PFD	process flow diagram
RFG	recirculated flue gas
SC	supercritical
SCR	selective catalytic reduction
SNCR	selective non-catalytic reduction
SNG	synthetic natural gas
TDP	technology development plant
TEA	triethanolamine
TKO	thermo-kinetics optimisation
TPRI	Thermal Power Research Institute
TRL	technology readiness level
TSA	temperature swing adsorption
UCG	underground coal gasification
US DOE	United States Department of Energy
USC	ultra-supercritical
WEO	World Energy Outlook (IEA)
WGS	water gas shift
WGC	warm gas clean-up
ZEP	zero emissions platform

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I Introduction

Coal is used to generate around 40% of the world's electricity and is expected to maintain its dominant share for the foreseeable future. However, an important element in this will be the increasing deployment of Clean Coal Technologies (CCTs) and Carbon Capture and Storage (CCS); both are expected to play significant roles in helping create and maintain a sustainable global energy structure. Both will be major elements in maintaining the role of coal as a fuel for power generation and industrial applications around the world, and will form an essential part of an overall strategy needed to achieve the carbon reductions required for stabilising atmospheric CO₂ concentrations.

In 2010, global greenhouse gas emissions reached an all-time high (30.6 Gt), a 5% increase over the previously highest level of 29.3 Gt reached in 2008. Emissions came from all major fossil fuels (44% from coal, 36% from oil, and 20% from natural gas). There is, therefore, a huge challenge to reduce CO₂ emissions produced by the use of these fuels. At the moment, the goal of limiting global temperature rise to no more than 2°C is looking less attainable, although the greater deployment of CCTs and CCS would certainly contribute towards achieving this.

Global coal resources are considerable and spread widely and, at current rates of production, are sufficient to last for more than a century. Numerous studies have examined the outlook for global energy demand and concluded that, despite efforts to diversify, some of the world's biggest economies will continue to depend heavily on coal for many decades to come. In a number of developed and developing economies, coal is essential for the provision of an affordable and reliable electricity supply that underpins economic and social development. Although coal use has plateaued or declined in some of the older industrialised nations, its use continues to increase in the burgeoning economies of countries such as China and India, where it provides a secure source of affordable energy, particularly for power generation. The IEA World Energy Outlook (IEA WEO, 2011) suggests that under the New Policies Scenario, between 2009 and 2035, global coal use will increase by ~20%. The bulk of this increase will occur in non-OECD Asian countries. In the period up to 2035, strong economic growth is expected for the region. China's growth will average 5.7%/y and India's 5.5%/y. Much of the resultant energy demand will be met using coal. There is clearly a huge challenge to improve and maintain the quality of life for all nations whilst limiting the scale of CO₂ emissions. The WEO notes that the long-term outlook for coal markets, more than for the other fossil fuels, will depend markedly on government policies towards energy and the environment (especially in China, India and other emerging economies) and how they affect the pace of investment into CCTs and CCS.

Globally, there are a number of ongoing major CCT and CCS programmes. In the case of the latter, there is particular emphasis on minimising the economic and efficiency impacts of deploying such systems on coal-fired power plants. Thus, for instance, the US Department of Energy has a goal of having technologies developed by 2012 that have advanced beyond the pilot scale and are ready for large-scale field tests. These must achieve 90% CO₂ capture at an increase in the cost of electricity of less than 20% for post-combustion and oxy-combustion, and less than 10% for pre-combustion capture (Figuerola and others, 2008). Similar aims are being pursued elsewhere.

The present report seeks to provide an update of the most promising coal-based CO₂ capture projects at significant scale being developed around the world. It summarises the latest data being produced from larger-scale (predominantly larger pilot-/demonstration-scale – TRL-6 or above projects (*see* the Appendix) and attempts to determine where gaps in the knowledge remain and how these are being filled. Where appropriate, recent data from smaller-scale (0.1–5% of full-scale – TRL-6) projects are also noted.

The focus is on the three main approaches to CO₂ capture, namely pre-combustion chemical capture from IGCC-derived syngas, post-combustion chemical capture using amines, amino acids or

ammonia, and oxyfuel combustion. Issues and technologies associated with CO₂ transport and storage fall largely outside the scope of this report.

As in other fields, complications can sometimes arise with the terminology applied to particular projects – there are a variety of different terms that are commonly used. Although there are several well recognised categories, descriptive terms are often used interchangeably. In theory, these should be self-explanatory. However, there is often little consistency in how different organisations and official bodies use them. Thus, projects may be described as being laboratory or bench scale, sub-pilot scale, pilot scale, demonstration or pre-commercial scale, commercial, industrial scale or utility scale. Descriptions can be further compounded by the use of terms such as small, medium and large.

Although a particular descriptive term (or a combination of terms) will generally impart a degree of understanding about a project, the distinctions between the different categories is frequently blurred.

Individual projects are frequently defined differently, often varying with organisations involved and place. This is particularly so where smaller-scale projects are described; for instance, virtually identical projects may be described alternatively as bench scale, large scale bench, or small scale pilot. Some may even be described as technology ‘demonstrations’.

In the case of pilot-scale projects, the Global Carbon Capture and Storage Institute (GCCSI) defines these as a process or technology that is being tested in a realistic environment, usually at one to two orders of magnitude smaller than a full-scale demonstration (GCCSI, 2010). To provide an indication of technology scale and maturity, the GCCSI suggests the use of Technology Readiness Levels (TRLs). The TRL approach can be useful in tracking the status of individual technologies and projects, particularly in the earlier stages development (*see* the Appendix). For instance, a pilot scale project (>5% of full-scale) would be rated at TRL-7 (GCCSI, 2011).

Confusingly, some other organisations often refer to pilot-scale projects as ‘demonstrations’. Again, definitions vary, although a demonstration plant is usually viewed as the final pre-commercial development step during which any outstanding issues are resolved (commercial plant design, avoiding technical risks, component integration, etc) (Schwendig, 2009). However, although such terms are used widely, when applied to clean coal technologies (CCTs) and carbon capture and storage (CCS), there is often a degree of subjectivity involved, and there are no universally-applied rules as to what constitutes bench, pilot, demonstration, and commercial scale.

Thus, the scale of a project can sometimes be addressed in a variety of ways. In the case of CCS projects, ‘scale’ may be described in MW_{th}, MW_e, or the amount of CO₂ capture anticipated. Some sources suggest that the upper limit for a pilot plant is around 30 MW (Bellona, nd), but there appears to be no universally accepted distinction between categories. For instance, the IEA CCS Unit describes a number of projects having CO₂ capture rates of between 20 and 100 kt/y as ‘pilot’ scale, with ‘commercial’ scale assumed to be in excess of 1 Mt/y (Finkenrath, 2011). However, in the USA, various projects in the range 400 kt/y – 3 Mt/y are referred to as ‘demonstrations’ (Wright 2011). Some US organisations (such as the National Mining Association) define large-scale demonstrations as capturing at least 1 Mt/y CO₂. In the UK, as part of the UK Government’s carbon capture competition, ‘commercial’ scale has been defined as demonstrating capture of about 300–400 MW. The GCCSI defines larger-scale coal-based CCS projects (LSIPs – large-scale integrated projects) as ones that involve the capture, transport and storage of CO₂ at a scale of not less than 800 kt/y.

Often, a degree of subjectivity is involved. This has been acknowledged by organisations such as the CSLF (Giove, 2011). They have suggested that:

- laboratory-scale/bench-scale would be less than 500 kW_{th} or 1000 t/y of CO₂ captured;
- sub-scale pilot would be less than 50 MW_{th} or 200 kt/y of CO₂ captured;
- full-scale demonstration would be >50 MW and/or >200 kt/y of CO₂ in any combination of capture, transport and storage;

-
- large-scale integrated demonstration would be >100 MWth and/or >200 ktCO₂/y with full transport solution and storage, including permitting and public outreach; more than 20% public funding;
 - a commercial project would be one initiated by industry to reduce emissions from a plant, with less than 20% public funding.

In the USA and China, there are several coal-fired power plants that capture ~200 t/d of CO₂ (equating to ~73 kt/y). In each case, the captured CO₂ is used for a range of commercial or industrial applications. Even though they are undeniably ‘commercial’ projects, under some classification systems they would be regarded as pilot scale.

The present report attempts to make clear the scale and nature of each project noted, and to avoid any confusion surrounding the use of the various terms adopted. It concentrates predominantly on what would, under most categorisation systems, be termed pilot and demonstration scale projects and activities. Where appropriate, Technology Readiness Levels, as defined by the GCCSI, are noted for individual projects.

2 CO₂ capture technologies for coal-fired plants

Historically, coal plants have been responsible for the emission of a number of pollutant species such as SO₂, NO_x and particulates. Gradually, technical solutions have been developed and applied widely to control these. However, in recent years, growing concerns over the possible impacts of global warming have re-focused attention on ways to reduce emissions of CO₂ from coal-fired processes. A wide range of different approaches is being pursued for possible application to coal-fired power plants and industrial applications. Some carbon capture techniques potentially suitable for such applications are at early stages in their development whereas others have been long-established, albeit in other industrial sectors. At one extreme, there are numerous small-scale projects still in the early phases of R&D, whereas at the other, a few larger-scale demonstration plants are now in operation. Many other projects and programmes fall somewhere between these extremes.

Although the range of possible CO₂ control strategies and systems under development continues to grow, at the moment, there are three general concepts that have progressed to the pilot and/or demonstration stage. These comprise:

- pre-combustion capture;
- post-combustion capture;
- oxyfuel combustion.

Each category encompasses a number of different alternatives or sub-categories, reflecting the differing approaches being taken forward by individual technology developers and utilities. Most have been reported widely elsewhere so within the present report, technical details provided are brief. Instead, for each technology stream, emphasis is placed on reviewing the current status of larger-scale projects, RD&D activities under way or planned, identification of gaps in the knowledge/requirements for further development, and the technical challenges still requiring resolution prior to system deployment.

A number of CO₂ capture systems have been in commercial use for many years; for instance, CO₂ separation/capture is undertaken regularly within the oil, gas and chemical industries. Furthermore, several small coal-fired power plants currently capture CO₂ from a proportion of their flue gases for subsequent commercial use. Even so, many of the capture solutions available or under development have their roots in various non-power uses and were not developed specifically for coal-based power generation. Most existing technological options require further development or modification to make them fully suitable for application to large-scale coal-based processes. For power generation and industrial applications (such as cement, and iron and steel manufacture) that rely heavily on coal, a key challenge is modifying and transferring suitable CO₂ capture processes that have proven commercially successful in other industrial sectors.

The conditions experienced in a typical coal-fired power plant are likely to be significantly different from those encountered in non-coal-based industrial processes (such as natural gas and refinery gas sweetening, and purification of ammonia and hydrogen plant synthesis gas) that feature carbon capture. The practical recovery of CO₂ from coal-derived flue gas is sufficiently different from other gas treating applications that it requires its own specialised processes. Thus, candidate technologies must be active at low CO₂ partial pressure and be tolerant to oxygen and various pollutant species present in coal-derived flue gas. The main process characteristics are summarised in Table 1.

Potentially, CO₂ produced by coal-fired processes can be captured in a number of ways. Absorption-based processes encompass the use of both chemical (amines, caustics, amino acid salts) and physical solvents (such as Selexol™ and Rectisol®). Adsorption-based systems include chemical (TSA) processes (metal oxides, metal organic frameworks) and physical (PSA, TSA) processes (zeolites, activated carbons, Si/Al gels). There are also other processes such as oxyfuel combustion, membrane

Table 1 Process characteristics for CO ₂ capture from coal-fired plants	
Characteristics	Issues
Low CO ₂ partial pressure	Flue gases have very low CO ₂ partial pressures because they are usually close to atmospheric pressure, with CO ₂ concentrations typically 3 –13 vol%. Commercial absorbents active enough for recovery of dilute CO ₂ from atmospheric pressure gas include amines and ammonia-based systems
Regeneration energy	Absorption processes most effective at low pressure are those with higher reaction energies that require the most regeneration energy. A major design challenge is to minimise regeneration energy
Oxygen	Oxygen can cause corrosion and solvent degradation problems. Carbon steel is desirable from a cost standpoint, but it can corrode rapidly in the presence of oxygen, especially in H ₂ S-free CO ₂ recovery systems. Some uninhibited amines can degrade excessively in the presence of oxygen
SO ₂	Some flue gases can contain significant concentrations of SO ₂ . This can react irreversibly with amines to produce non-reclaimable corrosive salts, detrimental to plant operation. Some coal boilers produce concentrations of 300–5000 ppm before FGD. For CO ₂ capture, levels of ~10 ppm SO ₂ are generally preferred
Fly ash	Fly ash in the CO ₂ absorption solvent may cause foaming in absorbers and strippers, scaling and plugging of equipment, erosion, corrosion, and increased solvent loss through chemical and physical degradation association with removed sludge. A removal efficiency of about 99.7 wt% is required to treat coal-derived flue gas
NO _x	NO _x can produce corrosion of steel and amine degradation in some plants
High flue gas temperature	Hot flue gases can cause solvent degradation and decrease absorber efficiency. Depending on the system, flue gas may need cooling prior to entering the absorber

capture (both organic and inorganic membranes), cryogenics, chemical looping, and CO₂ hydrates (Jones, 2007). However, only some of these have progressed to at least the pilot scale development stage or beyond.

In the following sections, the status of the three main technology streams is addressed, primarily via an examination of the larger-scale projects proposed, being developed or already active. Where appropriate, data generated from smaller scale testing is noted, especially where this is feeding directly into ongoing programmes aimed at developing further or scaling-up the particular technology.

2.1 Pre-combustion CO₂ capture

This section reviews the progress of larger-scale pre-combustion capture projects and summarises the major RD&D activities ongoing. The main development focus is to reduce costs involved. Some of the aims being pursued are similar to those for post-combustion capture, in as much as they involve the same basic concepts for new or improved capture processes. Improvements to various major IGCC plant components are also being sought, many of which will have a direct or indirect impact on CO₂ capture costs. There is ongoing development of plant components such as the air separation unit (ASU), gasifier, water-gas shift (WGS) reactor, and gas turbines.

Generally, in a coal-based process, CO₂ is recovered from a process stream following a gasification stage. This offers some advantages as the CO₂ is not diluted by combustion air and the CO₂-containing stream is usually at elevated pressure. Potentially, several different separation

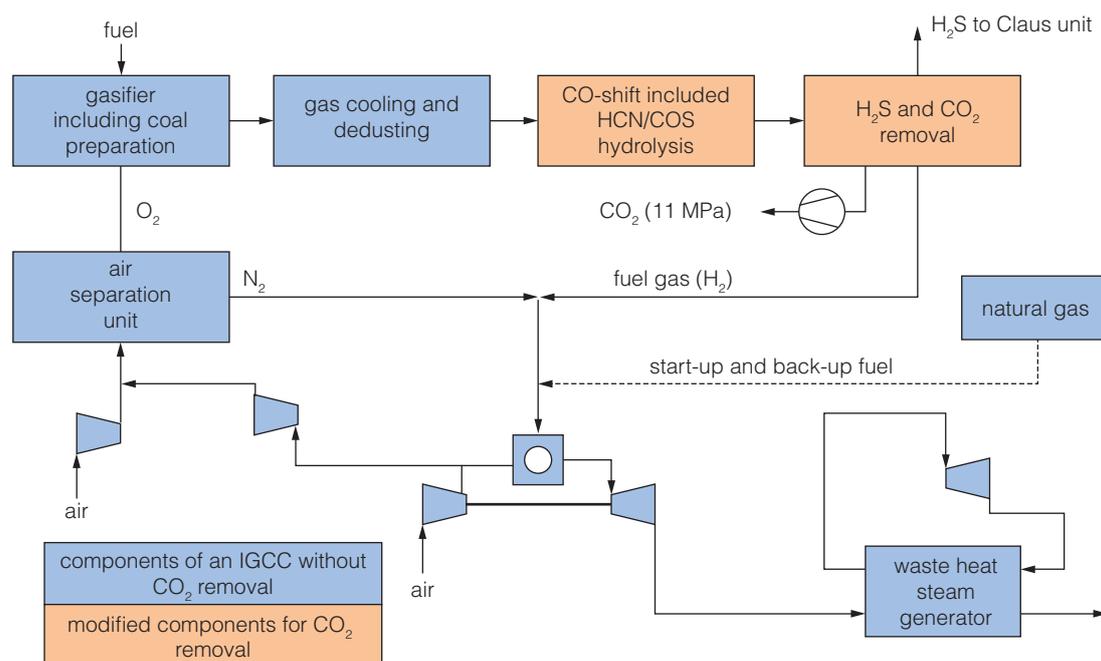


Figure 1 Process schematic for pre-combustion (Meyer and others, 2005)

techniques can be applied. Pre-combustion capture is generally viewed as being the most suitable for coal-fuelled IGCC plants. Here, coal is first gasified to produce a syngas, essentially a mixture of carbon monoxide (CO) and hydrogen, followed by the conversion of the CO to CO₂ ('shifted') by means of a water-gas shift reactor. Finally, the CO₂ is separated by conventional methods (a generic example is shown in Figure 1).

Technologies for pre-combustion capture of CO₂ as part of a gasification process are well established in industrial sectors such as hydrogen and ammonia production, oil refining, and methanol synthesis. In these processes, the ultimate capture of the CO₂ is usually accomplished under pressure by an acid gas removal (AGR – removing CO₂, H₂S and COS) process of absorption in a solvent, followed by regenerative stripping of the rich solvent to release the CO₂. This is then compressed and sent for storage or utilised for commercial process such as enhanced oil recovery (EOR). In pre-combustion capture processes, energy is expended at several stages. These include operation of the air separation unit, the loss of chemical energy due to the associated shift reaction, the addition of heat (steam) to the syngas to increase the water content prior to the shift reaction, and compression of the captured CO₂ (Ploumen, 2012).

There are two main generic types of AGR solvents, namely chemical and physical. Chemical absorbents (such as amines) react with acid gases and require heat to reverse the reactions that lead to their subsequent release. These processes generally have lower capital costs for AGR than physical solvents, but use larger amounts of steam-heat for solvent regeneration. Physical absorbents (predominantly Selexol™ and Rectisol®) dissolve acid gases preferentially with increasing pressure. The level of capture achievable depends on the individual solvent, the partial pressure of CO₂ in the gas stream, and the temperature; higher partial pressures and lower temperatures are more favourable (Figueroa and others, 2007). The absorbed gases are released from the solvent when pressure is decreased and temperature increased. Significantly less steam-heat is required for solvent regeneration than with chemical solvents.

Physical solvents tend to be favoured over chemical solvents when the concentration and partial pressure of acid gases or other impurities is very high, and are generally deployed for coal-based gasification and IGCC-type applications. Unlike chemical solvents, physical solvents are non-

Table 2 Advantages and disadvantages of pre-combustion capture (Figueroa and others, 2008; GCCSI, 2012e)	
Advantages	Challenges/barriers to implementation
Technologies for pre-combustion capture of CO ₂ via gasification are well established in the process industries Capture using the water-gas shift reaction and removal of the CO ₂ via AGR processes is used widely	Lower (but still significant) energy loss compared to post-combustion capture
As a smaller reaction volume is involved, at lower volumetric flow rates, elevated pressure, and higher component concentration, the CO ₂ separation step consumes less energy than post-combustion capture CO ₂ capture under pressure incurs lower energy penalty (~20%) than current post-combustion capture (~30%) at 90% capture	Capital costs of IGCC without capture are much higher than supercritical pulverised coal without capture IGCC costs need reducing to compete more effectively
Syngas contains high concentration of CO ₂ and is at high pressure, resulting in: – high CO ₂ partial pressure; – increased driving force for separation; – more technologies available for separation; – potential for reduction in compression costs/loads	Barriers to commercial application of gasification/IGCC are common to pre-combustion capture – availability; – cost of equipment; – extensive supporting systems requirements
Syngas produced as the first step of the process can be used to fuel a turbine cycle	Applicable mainly to new plants as relatively few coal gasification-based plants are in operation
Lower water use compared to post-combustion capture	
Large-scale plant (Kemper County plant in Mississippi, USA) becoming operational in 2014	

corrosive, generally requiring only carbon steel construction (Burr and Lyddon, 2009). The leading providers of AGR processes for CO₂ capture comprise (GCCSI, 2012c):

- Dow and BASF – MDEA (N-methyldiethanolamine);
- UOP – Selexol™;
- Lurgi/Air Liquide; and Linde – Rectisol®.

A major advantage of pre-combustion carbon capture is that the CO₂ separation step consumes much less energy than alternative processes as it takes place in a smaller reaction volume and at lower volumetric flow rates, at elevated pressure, and higher component concentration (Table 2). The higher concentrations make the capture process less energy-intensive and help reduce capital equipment costs. The energy generation penalty (typically 10–16%), is roughly half that of post-combustion CO₂ capture (Susta and Luby, 2007). Although the initial fuel conversion steps are more elaborate and costly than in post-combustion capture systems, the high concentrations of CO₂ produced by the shift reactor and the high pressures often encountered in these applications are more favourable for CO₂ separation.

However, to date, there has been only limited application at larger scale, which results in some technical and economic uncertainty (Figueroa and others, 2008). However, there are currently several pilot-scale projects planned or under way at coal-fuelled IGCC plants (*see* Section 4).

Table 3 Advantages and disadvantages of physical sorbents (Jones, 2007; Folger, 2010)	
Advantages	Disadvantages
Low utility consumption	CO ₂ pressure is lost during flash recovery
CO ₂ recovery does not require heat to reverse a chemical reaction	Necessary to cool syngas for CO ₂ capture, then heat and re-humidify for firing in gas turbine
Common for solvent to also have high H ₂ S solubility, allowing for combined CO ₂ /H ₂ S removal	Low solubility can require circulation of large volumes of solvent. This increases energy required for pumping
Rectisol® uses inexpensive, easily available methanol	Some H ₂ may be lost with captured CO ₂
Methanol used in Rectisol® process is non-corrosive so carbon steel can be used for most plant equipment	Refrigeration is often required for the lean Selexol™ solution
Refrigeration costs can be high	
Selexol™ has a higher capacity to absorb gases than amines	More economical at high pressures
Selexol™ can remove H ₂ S and organic sulphur compounds	Hydrocarbons are co-absorbed in Selexol™, resulting in reduced product revenue and often requiring recycle compression
Both provide simultaneous dehydration of the gas stream	
Both can remove both CO ₂ and various contaminants in a single process	

The two most widely used commercially-available physical capture solvents are Selexol™ and Rectisol® (*see below*). Both are used successfully for bulk removal of CO₂ (Burr and Lyddon, 2009; Tennant, 2011). The advantages and disadvantages of physical sorbents are summarised in Table 3.

Syngas produced during the coal gasification step is usually cleaned in two stages. Initially, it is quenched and cooled/washed, and dust, halides, cyanide and tars removed. After passing through a water gas shift reactor, it is again cleaned to remove H₂S and CO₂. This acid gas cleanup stage can use either the Selexol™ or Rectisol® process. Both processes can be tuned to generate separate streams of H₂S and CO₂, easing handling and transport.

Selexol™

The Selexol™ process has been in use for nearly 40 years. It uses a mixture of dimethyl ethers of polyethylene glycol (DMPEG) to absorb CO₂ and acid gases from syngas at relatively high pressure (usually between 2 and ~14 MPa). The acid gases are released using a pressure swing or steam stripping. Selexol™ has a number of properties that make its use attractive in commercial scale applications (Tennant, 2011). These include:

- a very low vapour pressure that limits its losses;
- a low viscosity that avoids large pressure drop;
- no heat of reaction and small heat of solution;
- chemically inert, thermally stable, and no oxidation degradation;
- non-toxic for environmental compatibility and worker safety;
- non-corrosive to carbon steel construction due to its non-aqueous nature and inert chemical characteristics;
- non-foaming for operational stability;
- high solubility for HCN and NH₃ allows removal without solvent degradation;
- high solubility for nickel and iron carbonyls allows for their removal from the syngas;
- low heat requirements for regeneration as the solvent can be partially regenerated by a simple pressure let-down.

Globally, there are nearly 60 Selexol™ units operating in syngas and natural gas service. This includes a number of IGCC plants in operation at oil refineries in the USA, Germany, Italy and France. Selexol™ was also used on the coal-fuelled Cool Water IGCC plant in the USA and is currently used on a number of petcoke gasification-based chemical producing plants such as Farmland Industries ammonia plant at Coffeyville in the USA.

In recent years, there have been a number of proposals for coal-fuelled IGCC plants that incorporate CO₂ capture based on Selexol™. The majority of these are in the USA although several others are also being developed elsewhere. In The Netherlands, Nuon/Vattenfall's 253 MW Buggenum IGCC plant is hosting a pre-combustion pilot-scale project. Data produced will be used eventually for the company's proposed larger scale Magnum IGCC project. The pilot plant has been designed to treat 0.8% of the syngas produced by the Buggenum plant and to capture approximately 10 ktCO₂/y. Selexol™ is used for CO₂ capture.

Activities are not limited to IGCC plants. For instance, at Medicine Bow, Wyoming, in the USA, a coal-to-transport fuels plant producing up to 21,000 bbl/d of gasoline has been proposed. This will use GE gasification technology. Around 3.6 MtCO₂/y will be captured using Selexol™ pre-combustion technology, followed by pipeline transport for EOR application in the Denbury oil fields. Similar CTL plants are also proposed in different parts of the world.

Rectisol®

This was first applied commercially in 1949 and is the most widely used physical solvent gas treating process; more than 85 plants are in operation. Most impurities and trace contaminants can be removed in a single absorption process; chilled methanol is used to absorb H₂S and CO₂, usually at a pressure of between 2.7 and 7 MPa. In the first stage of stripping, the methanol provides bulk removal of CO₂ and near complete removal of H₂S and COS. In the second stage, remaining CO₂ and residual sulphur compounds are removed. The process also removes HCN, NH₃, and nickel and iron carbonyls. The various compounds are desorbed by reducing the pressure of the solvent, stripping, and if necessary, reboiling the solvent. The solubility of the different compounds being removed in the methanol solvent varies considerably, thus H₂S and CO₂ can be removed selectively. Typically, the gas produced is very pure, with total sulphur content <0.1 ppmv, and CO₂ <2 ppmv. A pure CO₂ stream can be produced suitable for EOR or chemical synthesis. The advantages and disadvantages of Rectisol® are summarised in Table 4.

The Rectisol® process has been used successfully to treat syngas produced by a number of different coal gasification processes such as Lurgi fixed bed, British Gas/Lurgi, Shell, and GE (formerly Texaco) gasification. There are a number of coal-based plants in operation that incorporate the Rectisol® process for gas cleanup and/or CO₂ capture. Most are on coal gasification plants in China producing chemical feedstocks such as methanol, urea and ammonia. A number of others are being built and expected to be on line by 2012. One of the largest coal-based plants currently employing Rectisol® is the Great Plains Synfuels plant in North Dakota, USA (see Section 2.3.1).

Table 4 Advantages and disadvantages of the Rectisol® process (Tennant, 2011)

Advantages	Disadvantages
Selectivity for H ₂ S over CO ₂ is high - only slightly less than Selexol™	Complex process scheme
Solubilities of H ₂ S and COS higher than in Selexol™	Need to refrigerate solvent
Allows for deep sulphur removal to <0.1 ppmv H ₂ S + COS	Leads to high capital and operating costs
High selectivity for H ₂ S combined with ability to remove COS	Relatively high vapourisation losses of the solvent even at low temperatures due to the appreciable vapour pressure of methanol
Also absorbs HCN, NH ₃ , and iron-and nickel carbonyls	
Applicability to deep cleaning of syngas for catalytic conversion (sensitive to contaminants) for such products as ammonia, hydrogen, and F-T liquids	

2.2 IGCC pre-combustion capture projects

2.2.1 Willem-Alexander IGCC plant, Buggenum, The Netherlands

In June 2011, Vattenfall/Nuon officially opened its Buggenum CCS pilot plant. This operates on a 20 MW slipstream (TRL-7) from the existing 253 MW IGCC plant (*see* Figure 2) and captures ~90% CO₂. The pilot plant consists of five sections: syngas conditioning, water-gas-shift condensate recovery, CO₂ absorption and solvent regeneration, and CO₂ compression. CO₂ capture is carried out using dimethyl ether polyethylene glycol (Selexol™) as a physical solvent. As no suitable reservoir is available, CO₂ released from the capture solvent is compressed and mixed together with the hydrogen-rich stream emerging from the top of the absorber. It is then fed back to the power plant via the syngas line and then to the gas turbine.

The ongoing R&D programme supporting the project involves Vattenfall/Nuon, ECN, Delft University of Technology, TNO, KEMA, and the Dutch government. There are three main objectives:

- to demonstrate operation of the integrated components;
- to verify whether the predicted performance is realistic;
- to acquire operational experience (for instance, during part-load operation).

There are four main work packages under way that encompass plant operation and optimisation, water gas shift operations, CO₂ absorption, and fouling and corrosion issues. As part of this test programme, modelling activities and catalyst experiments are being undertaken. The programme is proceeding via several test campaigns. These began in 2011 and are examining different catalysts, solvents and



Figure 2 The Willem-Alexander IGCC plant, Buggenum, The Netherlands (photograph courtesy of Nuon/Vattenfall)

packings. This phase is expected to last for two years with the capture pilot plant being operated under varying conditions whilst using different WGS catalysts and physical capture solvents. The programme is expected to generate data useful for scaling-up the technology for eventual deployment at the proposed 1200 MW multifuel Magnum IGCC plant being developed by Vattenfall/Nuon in Eemshaven (currently on hold). It is anticipated that the ongoing RD&D programme will help reduce significantly CO₂ capture costs.

2.2.2 ELCOGAS, Puertollano IGCC plant, Spain

Pre-combustion CO₂ capture processes are not limited to physical solvents, and in Spain a different approach has been adopted at the 335 MW Puertollano IGCC plant (*see* Figure 3). In 2010, an amine-based 14 MWth pilot (TRL-6) CO₂ capture plant was commissioned. This has the capability of capturing up to 35 kt/y of CO₂, whilst producing 700 t/y of pure hydrogen. The pilot plant treats 2% of the syngas from the existing IGCC power plant.

The pilot plant comprises a shift unit, a CO₂ separation unit based on amine absorption, and a



Figure 3 The Puertollano IGCC plant (photograph courtesy of ELCOGAS)

hydrogen purification unit. Auxiliary and control systems are all integrated into the IGCC facility. Syngas can be fed to the pilot plant either desulphurised (from downstream of the IGCC's desulphurisation unit) or from upstream. During the CO₂/hydrogen separation stage, an aMDEA (active methyldiethanolamine) solution is used for CO₂ capture. Downstream from this, the resulting gas is hydrogen enriched to produce 'raw hydrogen' (~77% purity).

This can be fed to the gas turbine or further purified in the next pilot plant step. Pure hydrogen (99.99%) can be produced from the raw hydrogen by means of a pressure swing adsorption (PSA) unit. Impurities such as CO₂, CO, N₂ and Ar are retained in a multi-bed adsorption system while the hydrogen passes through it. The aMDEA is regenerated by means of temperature increase and pressure reduction.

Project funding has been provided by the state and regional governments and the industrial owners of ELCOGAS (ENDESA, EDF, Iberdrola, Hidrocarbónico, ENEL, EDP, Siemens, BWE, and Krupp Koppers). The University of Castile-La Mancha and Spanish research institutions INCAR-CSIC and CIEMAT are also involved in the project which forms part of a national strategic research programme (PSE-CO₂) aimed at developing and demonstrating the technical and commercial feasibility of large-scale CCS.

The pilot plant started operation in late 2010. A major aim has been to validate, at industrial scale in an existing commercial IGCC, hydrogen co-production and CO₂ capture (from coal and petcoke), integrated with electricity production. Process testing and optimisation has been undertaken to provide technical reliability data regarding process economics and efficiency. WGS catalyst optimisation has been examined, and a number of different catalysts evaluated. By mid-2011, pilot plant testing had generated useful operational data (Davidson, 2012). It was determined that:

- investment costs were less than €3 million;
- there was unexpected reactivity in the first step of the shift unit; it may be possible to carry out the shift process in a single step;
- achieving design specifications of the main streams was easily accomplished (CO₂ > 99.6% and pure H₂ of >99.995%);
- auxiliary power consumption was lower than estimated in design;
- integration of operations and maintenance in the existing IGCC was easy;
- the rate of CO₂ capture was 91.7%;
- cold gas efficiency was 89.5%;
- initial estimated cost of avoided CO₂ was ~20–28 €/t.

Characterisation tests ended in June 2011. It is anticipated that sufficient technical and economic data had been generated to support scale-up of the process.

Now that this particular test programme has been completed, ELCOGAS is offering the pilot plant as an RD&D platform. This will allow various activities to be pursued. Proposals for future projects include:

- optimisation of shift catalysts and testing of different types;
- development and demonstration of new processes for CO₂-H₂ separation;
- increased overall efficiency through improved integration between the CO₂ capture facility and the IGCC power plant;

- integration of commercial hydrogen-based processes, in addition to power co-production;
- comparison of advantages and disadvantages of acid and sour catalysts;
- improved synergy between CO₂ capture and storage;
- testing of alternative capture technologies, currently being developed at small scale.

2.2.3 TECO Polk IGCC, Florida, USA

A project is under way on the 320 MWe Unit 1 of Tampa Electric's IGCC power plant (*see* Figure 4) that will evaluate a combination of syngas clean-up and CO₂ capture (the *Warm Gas Cleanup (WGC) and CCS Demonstration*). A DOE co-operative agreement was put in place in 2010 to demonstrate



Figure 4 TECO Polk IGCC plant in Florida (photograph courtesy of TECO)

RTI's Warm Gas Cleanup sulphur removal technology at the plant, which cleans syngas at elevated temperatures. This was followed by the announcement of DOE support for the addition of CCS to the existing WGC project. The project partners include the US DOE/NETL, RTI International, TECO, Shaw Group, Sud-Chemie, BASF Group, and the Eastman Chemical Company.

The new development will involve the addition of a shift reactor (sweet shift) and syngas cooling systems (Hornick, 2011; Hopf and others, 2011). RTI will design, construct,

commission and operate the 50 MWe test facility (TRL-6) that will treat around 20-30% of the IGCC plant's syngas output. Following the water gas shift reactor stage, the syngas will be cooled and fed to a carbon capture plant using BASF activated MDEA. This was selected because of its reportedly lower capital cost and energy use, and its ability to capture up to 90% of available carbon in the syngas slipstream. Up to 300 kt/CO₂y will be captured. Specific project goals include an 8000-hour operating programme, >90% trace contaminant (Hg, As, Se) removal, and >90% CO₂ capture. The latter will be stored in a saline aquifer 1500 m beneath the Polk power plant.

FEED activities are currently under way. The schedule suggests that engineering, procurement and construction for the project will take place between 2011 and 2013, with commissioning and operation between 2013 and 2015. Key critical technical issues flagged up include optimisation of the shift reactor, and operation of the GE 7FA gas turbine on hydrogen-rich syngas (Gupta and others, 2010). It is anticipated that the system has the potential to reduce significantly the capital and operating costs of an IGCC plant equipped with carbon capture technology.

2.2.4 Kemper County IGCC, Mississippi, USA

The IGCC plant in Kemper County is being built by Mississippi Power Company, a Southern Company subsidiary. Engineering is a joint effort between KBR and Southern Company Services, which is undertaking procurement and construction management. The project will generate 582 MW at peak and 524 MW fired on syngas, producing ammonia, sulphuric acid and CO₂ as by-products.

The plant has two separate gasification trains, each of which will consume 575 t/h of raw local lignite. Each will supply syngas to a single combustion turbine and heat recovery steam generator (HRSG).

Both trains will have three parallel coal drying and milling units feeding into two high pressure coal feed systems. There will be two process air compressors per gasification train. Syngas produced will be cooled, cleaned of particulates then scrubbed with water in a syngas scrubber to remove halogens and other contaminants and to saturate the syngas to facilitate the shift reaction. Around 90% of the CO in the syngas will be shifted to CO₂ to increase its partial pressure. This will help reduce station services required for the Selexol™ unit and also to meet CO₂ pipeline purity requirements. The shifted sour syngas will pass through a COS hydrolysis reactor and be routed through an ammonia scrubber and a Selexol™ acid gas removal unit to remove sulphur and CO₂, followed by a mercury removal bed. It will then be fed to the gas turbine.

The project will capture ~65% of the CO₂ produced (TRL-9), putting its emissions on a par with natural gas fired combined cycle power plants. The CO₂ compressor system will compress ~11 kt/d of CO₂ (around 3 Mt/y) reportedly one of the largest CO₂ compressors in the industry. The removed CO₂ stream will be dehydrated, compressed and sold for EOR.

In June 2010, the Mississippi Public Service Commission approved a certificate of convenience and necessity for the project, and work is now progressing through the design, procurement and construction phases. Most of the large-scale equipment procurement took place during 2010. Plant construction also began mid-2010 (Koneru and others, 2011). By the beginning of 2012, the project was in the detailed engineering and procurement phase, and construction was well under way. Engineering was scheduled to be completed by the first quarter of 2013, with commercial operations beginning by the end of 2014. However, in June 2012, it was announced that the project was running over budget and that costs had increased from US\$2.4 billion to US\$2.88 billion. As part of efforts to control costs, in August 2012, it was announced that the primary builder (a joint venture between KBR and Yates Construction) was being replaced by Performance Contractors. However, KBR will continue to perform engineering and start-up services for the project. The Kemper County project is viewed widely as the next key event for the advance of pre-combustion capture technology, with integrated operation of the first IGCC plant with CO₂ capture.

2.2.5 Nakoso IGCC Demonstration Plant, Japan

The 250 MW Nakoso IGCC plant is operated on a commercial basis by the Clean Coal Power R&D Co Ltd. It is based on technology from Mitsubishi Heavy Industries Ltd (MHI) and uses a pressurised, air-blown, two-stage, entrained-bed coal gasifier with a dry coal feed system. The syngas produced passes through a combined char/particulate removal and initial cooling unit, and is then cooled further in several heat exchangers en route to the gas turbine. Before feeding to the combustor inlet, the fully cooled syngas is passed through an unconventional COS converter (using MHI's proprietary honeycomb catalyst that completes the COS shift reaction without the addition of steam) and chemical absorber unit for H₂S removal using MDEA solvent. A feasibility study to execute a CCS demonstration project at the plant was begun in April 2008. It is proposed that CO₂ will be captured using amine-based technology developed in-house. It will then be transported by pipeline some 70 km for storage in depleted reservoirs in the Iwaki Gas Field, operated by Inpex. The Nakoso plant was flooded during the 2011 tsunami but came back on line in July of the same year. It has since been operating continuously on full load and progress has resumed.

2.2.6 Vresova IGCC, Czech Republic

Although not originally designed as such, the 400 MWe power plant operated by Sokolovska uhelna, pravni nastupce, a.s. (Sokolov Coal Corporation, SUAS) located at its Vresova gasworks has for more than 16 years been operating as a coal-fired IGCC.

Twenty six Lurgi-type fixed-bed gasifiers process brown coal from the company's own local opencast

mines. The raw syngas produced exits the gasifiers at a pressure of 2.7 MPa, is cooled progressively to ~30°C, then washed with a mixture of water and hydrocarbons to remove crude naphtha, ammonia, HCN and any ash remnants. The cleaned gas is then fed to a Rectisol® unit where mainly H₂S and COS are removed. The pressure of the clean syngas downstream of the Rectisol® unit is 2.1–2.5 MPa, which allows it to be used in two GE 9E gas turbines without additional compression. In the plant's original town gas application, the Rectisol® unit included a second stage, in which CO₂ was removed down to ~5% volume, although this stage is currently being bypassed. At the moment, most of the CO₂ is left in the gas so that it can perform mechanical work in the gas turbine expander section.

2.2.7 IGCC plants proposed or under development

A number of other coal-fuelled IGCC plants that feature carbon capture are at various stages in their development. These all plan to incorporate some form of pre-combustion capture although in some cases, the precise nature has not yet been made public (Table 5). One of the projects at an advanced stage of development is the Chinese 250 MW **GreenGen IGCC/CCS** project. Following completion of Stage I, the project will be enlarged to 650 MWe though the addition of a 400 MW unit. The expectation is that CO₂ capture will be included on the latter unit, with the resultant CO₂ used for EOR in the nearby Daquang oilfield. Syngas will also be sold for chemicals production. The 250 MW IGCC plant is expected to begin operation in 2012. The exact duration of the subsequent R&D operational programme for the plant (rather than commercial power generation) has not yet been finalised.

Other projects are less well advanced. For instance, in the UK, the 900 MW 2Co Power (Yorkshire) **Don Valley IGCC + CCS** project (formerly the Hatfield IGCC project) has now completed the FEED stage. This integrated power plant plans to use two Shell gasifiers and consume 2 Mt/y of coal. It will feature CO₂ capture (90%) (TR-9), transportation, and storage combined with EOR in the North Sea.

Captured CO₂ will be transported via a 175 km pipeline being developed by National Grid. Selexol™ will be used for acid gas removal and CO₂ capture (up to 5 Mt/y). In January 2012, it was announced that Foster Wheeler AG had been awarded a project management consultancy contract for the project. This will include development of the engineering, procurement and construction contract package and review of the existing FEED package. In March 2012, it was announced that Samsung was to take a strategic 15% stake in the project and was being appointed as EPC contractor. In June 2012, BOC joined the project, also taking a 15% share. BOC is working with the existing contractors to finalise the project's FEED. BOC's parent company, Linde, will supply air separation units as well as the CO₂ capture technology. A final investment decision for the project is expected in mid-2013. This will be subject to confirmation of financial support from the UK government and the European Union. If the project proceeds on schedule, 2Co expects the plant to begin operation by the end of 2016.

Also in the UK, C.GEN is proposing the **North Killingholme power project**. This 430 MW IGCC plant would be fuelled on combinations of hard coal, petcoke and biomass (woodchips). It is estimated that ~2.5 MtCO₂/y would be captured using pre-combustion capture technology. C.GEN anticipates that the project will rely on the common user pipeline infrastructure being developed by National Grid for the transport of CO₂ to deep saline formations and/or enhanced oil recovery. Elsewhere in the UK, the **Eston Grange CCS Plant** is planned by Progressive Energy. This will be a new-build 850 MW IGCC power plant using bituminous coal as a feedstock. It is expected to capture ~5 MtCO₂/y from a 400 MW slipstream; again, pre-combustion capture technology is proposed. Captured CO₂ will be piped off-shore for storage in deep saline formations. The project is scheduled to reach commercial operation in 2016. A new-build coal and biomass-based power station generating 1724 MW is also proposed by **Ayrshire Power** (Peel Energy, RWE npower). When operating at full scale, ~ 2 MtCO₂/y will be captured by three separation units. It is anticipated that this will be transported off-shore for storage in depleted oil and gas reservoirs. Ayrshire Power is in advanced stages of applying for consent from the Scottish Government to construct the facility. Preliminary

Table 5 Proposed coal-based IGCC projects featuring pre-combustion CO₂ capture (Folger, 2010; PEI, 2011; Davidson, 2012; <i>also</i> CCC internal sources)				
Project	Proposed start-up	Capacity, MWe	CO ₂ capture system	Annual CO ₂ capture, Mt
Texas Clean Energy Project (TCEP), Summit Power, USA	2015	400 (+ sulphuric acid, urea, CO ₂)	Rectisol®	2.7
Hydrogen Energy California Project (HECA), USA	2016	390 (+fertiliser)	Rectisol®	32.0
Tenaska, Taylorville Energy Center, Illinois, USA	2014*	716	Selexol™	1.9
Southern California Edison, Utah, USA	2017	500	Selexol™	3.5
AEP, Meigs County, Ohio, USA	On hold	629	Selexol™	1.5
Duke Energy, Edwardsport, Indiana, USA	2012†	630	Selexol™	1.5
Excelsior Energy, Mesaba, Minnesota, USA	2014*	603	Selexol™	3.0
Mississippi Power, Kemper County, Mississippi, USA	2014	582	Selexol™	3.5
Erora Group, Kentucky, USA	2015	720	na	2.0
EmberClear Corp, Good Spring, Pennsylvania, USA	na	270	na	na
Refined Energy Holdings, Idaho, USA	na	520	na	na
AEP, Mountaineer Station, West Virginia, USA	On hold	629	Selexol™	Phase I 100 kt Phase II 1.5 Mt
GreenGen, China	2011 (Stage I)	Phase I 250 Phase II 650	na	Phase II 30–60 kt/y
Lianyungang Clean Energy Innovation Park, Jiangsu Province, China	2015	1200 + syngas and chemicals	na	Up to 1 Mt/y from IGCC and adjacent USC PCC plants
Dongguan Taiyangzhou IGCC, China	na	750	na	Up to 1 Mt/y
Caledonia Clean Energy Project, Grangemouth, UK (Summit Power, National Grid, Petrofac)	2018	na	na	na
2Co Don Valley Project, UK	2016	900	Selexol™	4.5–5.0
C.GEN, Killingholme, UK	2015-16	520–570	Selexol™	~3.65
Eston Grange Power Project, UK	2016	800	na	5.0
Kedzierzyn, Opole, Poland	2015	309	na	2.4–3.4
Osaki CoolGen plant, Japan	2017	170	na	~73–90 kt
* project possibly shelved or on hold				
† no capture planned for delivery in 2012				

studies for the project were conducted in the fourth quarter of 2009, with feasibility studies started in March 2010. The project is scheduled to be operational in 2016.

There are also several major projects progressing in the USA. Summit Power Group is developing the

400 MW IGCC polygeneration **Texas Clean Energy Project (TCEP)**. In 2010, the project was awarded US\$450 million by the US DOE under the third round of its Clean Coal Power Initiative. Early in 2012, EPC contracts and operation and maintenance agreements were finalised with three EPC contractors (Siemens Energy Inc, Selas Fluid Processing Corporation/Linde Group, and major Korean contractor SK Engineering & Construction). Selas and SK Engineering are supplying a complete chemical block capable of producing syngas from the gasification of Powder River Basin coal. The chemical block EPC contract also includes coal handling, coal gasification using two Siemens SFG-500 gasifiers, gas clean-up, mercury removal, ammonia and urea production facilities, sulphuric acid plant, water treatment, and CO₂ compression unit. A portion of the syngas produced will fuel the Siemens power block, and the balance will be used for the production of granulated urea. The chemical block will capture 90% of the CO₂ from the syngas (using Rectisol®) and compress it for EOR purposes in the Permian Basin in West Texas. Some 2.7 MtCO₂/y will be captured. A CO₂ purity of up to 98.5% is expected. Reportedly, the project is currently at the FEED stage, with the start of operation scheduled for 2015. Alongside the Kemper County project, it will be one of the first coal-fired power facilities in the USA to combine IGCC with CCS (at TRL-9).

In March 2012, it was announced that Summit Power was also involved in a proposed IGCC + CCS plant to be located at **Grangemouth** in the UK (the *Caledonia Clean Energy Project*). It seems likely that the proposed plant would be similar in design to the TCEP project. Summit has joined with National Grid and the oil services company Petrofac for the Caledonia project. The consortium hopes to win funding from the UK government. CO₂ would be capture and piped to St Fergus in Aberdeenshire, then on for storage beneath the North Sea. A start-up date of 2018 has been suggested.

Also in the USA, the **Hydrogen Energy California Project (HECA)** 390 MW IGCC project in California will be fuelled on petcoke or blends of petcoke and coal. SCS Energy LLC, a US power development company, is developing the project. The plant will be built near Bakersfield in California's Central Valley and will use MHI's proprietary oxygen-blown gasification technology. A portion of the syngas generated will be used for the production of ~2500 t/d of fertiliser at the facility. Rectisol® will be used for CO₂ capture. Around 90% CO₂ capture is planned; this will amount to ~3 Mt/y. This will be piped to a nearby oil field and used for enhanced oil recovery. The project is currently in the permitting stage. Reportedly, construction could begin in 2012 with full-scale operation starting in late 2016. In June 2012, it was announced that MHI was to undertake the FEED study for the plant's the gasification and power island. This will be completed by March 2013. SCS Energy is expected to finalise the contract for EPC in mid-2013. Construction is slated for completion by the end of 2017.

2.3 Non-IGCC-based applications

Pre-combustion carbon capture is also being applied (or planned) for a number of other coal-based non-power processes.

2.3.1 Coal-to-chemicals

Globally, various coal gasification-based processes employ pre-combustion CO₂ removal as part of the process for producing ammonia, fertilisers, chemicals, and gaseous fuels such as hydrogen and methane. In the USA, there are several commercial gasification-based chemicals production facilities that separate CO₂. At Coffeyville, Kansas, ammonia and urea is produced via gasification although excess CO₂ vented; however, this particular plant gasifies petcoke. At Eastman Chemical in Kingsport, Tennessee, coal is gasified for the manufacture of methanol and other chemicals; again, CO₂ is mainly vented. There are also a number of other US projects still at various stages in their development. For instance, Faustina Hydrogen plans to build a coal gasification plant in Louisiana that will produce ~4000 t/d of ammonia and liquid products from the gasification of high sulphur coal and petcoke. It is

envisaged that 1.5 MtCO₂/y will be captured (although details of the proposed capture system have not yet been revealed) and used for EOR purposes. A plant start-up date of 2019 has been suggested.

Elsewhere, there are a growing number of coal-to-chemicals plants operating, particularly in China where coal-fuelled gasification plants produce syngas used for the production of chemicals and feedstocks such as DME, methanol, ammonia, urea, olefins, and fertilisers (Mills, 2010). At the end of 2011, there were around 116 coal gasification projects operating or in the design/construction phase. Most modern Chinese coal gasifiers currently in operation are of the entrained flow variety, although there are also a smaller number of fixed and fluidised bed units. Entrained flow gasification is favoured as it offers considerable fuel flexibility for the production of syngas, including the use of bituminous coals (rather than anthracite) in ammonia synthesis. The scale of operation is significant, typically up to 2 kt/d coal throughput per unit (NETL, 2010; Minchener, 2011). In many cases, CO₂ is separated from the syngas and simply vented. However, in some fertiliser plants, it is reacted with ammonia to form urea. For instance, over the last decade, Kellogg Brown Root (KBR) has supplied a number of pre-combustion CO₂ capture systems to Chinese chemical plants. In the future there may be opportunities for clusters of production plants to capture and combine their individual CO₂ outputs. This would reduce costs and could lead to large-scale technology demonstrations within China.

2.3.2 Coal-to-SNG

As a by-product of the process, and in a low carbon economy, the development of CCS will be a critical factor in the future development of the technology. In the absence of CCS and with a carbon allowance price, SNG may be expensive and not be economic. However, higher natural gas price and, where appropriate, the sale of CO₂ for EOR, could make the process economically viable.

At the Great Plains Synfuel Plant in North Dakota in the USA, is one of the world's biggest coal-to-SNG production facilities (*see* Figure 5). Here, local lignite is gasified in Lurgi gasifiers to produce SNG, with the separated CO₂ compressed and piped to the Weyburn and Midale oilfields in Canada for EOR (GCCSI, 2009). Fourteen Lurgi gasifiers convert 6 Mt/y of lignite to SNG, most of which is piped to Ventura for distribution in the eastern United States. A nickel based catalyst is employed in



Figure 5 The Great Plains Synfuel Plant in North Dakota, USA (photograph courtesy of Basin Electric)

the methanation process (Chandel and Williams, 2009) and Rectisol® is used to remove H₂S and CO₂. The plant typically generates more than 8000 tCO₂/d. Around half of the CO₂ produced when running at full rate is exported (~5.6 million m³/d); total supply is ~3 Mt/y. Great Plains captures more CO₂ from coal conversion than any other facility in the world and is a participant in the world's largest CCS project.

There are also a number of proposed coal-to-SNG plants that are likely to include CCS as part of their make up. In the USA, at least 15 commercial-scale coal-to-SNG plants have been proposed; all are at different stages of development. Some feature pre-combustion carbon capture and storage as part of their design. For instance, Secure Energy plans to build a plant in Decatur, Illinois, that will gasify 1.4 Mt/y of local coal to produce pipeline quality natural gas. If it proceeds, it is envisaged that this modular facility will act as a template for four similar plants being promoted by the company in other parts of the country. CO₂ captured will be utilised for various purposes. Similarly, at Leucadia,

Louisiana, the Lake Charles Cogeneration Company is building a commercial coal-to-SNG plant that is scheduled for completion in 2013. CO₂ captured from the process (~85% of the total) will be used for EOR operations in the Gulf Coast region. And in Muhlenberg County, Kentucky, ConocoPhillips and Peabody Energy are developing plans for an SNG plant ('Kentucky NewGas'). Coal will be supplied from large reserves adjacent to the site. The partners claim that the new plant will produce very low emissions. Reportedly, it will be built capture-ready and should it proceed, is expected to capture around 5 MtCO₂/y (~90% capture). This will be piped to nearby saline aquifers for storage. Preliminary testing indicates that storage potential is good. Opportunities for EOR are also being examined. A start-up of commercial operations of 2017 has been suggested. At Rockport, a US\$2.8 billion coal-to-SNG project is being developed by Indiana Gasification LLC. This recently received its air emissions permit. It is proposed that CO₂ captured from the process will be piped to the Gulf of Mexico for EOR use.

In South Korea, steel producer POSCO is constructing a major SNG plant in Gwangyang. This will be fuelled on 500 kt/y of coal and/or petcoke. ConocoPhillips' E-gas gasification technology is being used. Linde is supplying syngas treatment and conditioning technology, including sour shift, acid gas removal, and sulphur recovery. Acid gases and bulk CO₂ removal will be carried out using Rectisol®. Haldor Topsøe is providing the methanation technology, capable of producing SNG with a methane purity of >98%. The plant is scheduled to come on stream in 2013.

In February 2012, it was announced that GreatPoint Energy of the USA had completed a US\$1.25 billion deal to build a large-scale coal-to-SNG plant in China. As part of this collaborative effort, China Wanxiang Holdings will invest US\$420 million in GreatPoint Energy and will finance construction of the plant; the first phase is due for completion by 2015. According to the companies, when complete, the plant should produce ~840 billion m³ of SNG, representing about 0.5% of China's projected energy needs. Sinopec will build the pipeline infrastructure needed to deliver the gas produced to the eastern industrial and urban populations in China. CO₂ will be captured from the process and sold on for EOR. The two companies plan to establish a joint venture to develop further SNG plants in Asia and elsewhere.

2.3.3 Underground coal gasification (UCG)

The use of physical solvents for CO₂ capture is not limited to 'conventional' coal gasification-based processes. In Canada, a commercial underground coal gasification project (Swan Hills Synfuels) proposes to generate 300 MW of electricity and capture and utilise 1.3 MtCO₂/y for local EOR purposes. This will be removed using a physical solvent (probably Selexol™ or Rectisol®). The first phase of the project was completed successfully in July 2009. The FEED stage is now under way and should be completed by mid-2012. This will be followed by the start of construction, with the venture (including CCS) reportedly becoming operational in 2015 (ZeroCO₂, 2011; CSLF, 2011).

There are also a number of UCG + CCS proposals in other parts of the world. For instance, in the UK, licences for 18 UCG projects have been issued by the Department of Energy and Climate Change (DECC). One of these proposes accessing coal reserves beneath Swansea Bay, Wales; reportedly, these amount to over a billion tonnes. Should the project proceed, it is proposed that CO₂ would be captured and stored. A second UK-based proposal is being led by B9 Coal and promoted by an industrial consortium. The aim is to combine UCG with alkaline fuel cell technology. At least 90% CO₂ capture is envisaged. There are also various other European proposals that include a UCG + CCS project in Bulgaria where captured CO₂ will be stored on site underground. Funding is being provided by the European Commission's Research Fund for Coal and Steel.

There are a significant number of UCG projects proposed in parts of Asia, although currently, only some feature carbon capture as part of their design. For instance, a pilot/demonstration scale UCG + CCS facility is being developed in Inner Mongolia. Syngas will be used to supply a local power plant,

with CO₂ captured and stored in depleted coal measures. Coals will be gasified at a depth of >350 m and will include long flame coal and lignite. Reportedly, initial operation could begin in 2012 (Jade, 2010). There are also other proposed UCG projects in China, India, and Nigeria that could potentially, incorporate carbon capture.

2.3.4 Coal-to-liquids (CTL)

Carbon capture is also a feature of a number of proposed coal-to-liquids plants. Some of the more advanced projects are noted in Table 6. There are also others, mostly at the design or feasibility stage. However, in China, a major CTL project, the Shenhua Direct Coal Liquefaction (DCL) project in the Inner Mongolia Autonomous Region is now in operation. The project began its feasibility study in 2003 and in late 2008, the first of the two reactor trains of the first phase operated successfully. The plant has two trains using Shell gasifiers and has a capacity of 1 Mt/y of diesel and gasoline (7 million barrels). Following syngas shift conversion, the resulting gas mixture contains ~87% by weight of CO₂ (Minchener, 2011). Hydrogen can be separated from the CO₂ at comparatively low cost and is used in a hydrogenation process to produce synthetic oil. As part of China's first integrated industrial-scale CCS trial, some captured CO₂ is being diverted via a sidestream, treated, and compressed to produce a 99.2% pure liquid. This cryogenic liquid is then transported by road tankers

Table 6 Planned coal-to-liquids projects featuring full-scale pre-combustion CO₂ capture (Folger, 2010; Couch CTL; Finkenrath, 2011; *also* CCC internal sources)

Project	Proposed start-up	Capacity, bbl/d/MWe	CO ₂ capture	Annual CO ₂ capture, Mt/y
Baard Energy Clean Fuels, Ohio, USA	2015	53,000 + 250 MWe	Rectisol®	
DKRW Energy, Medicine Bow, Wyoming, USA	2014-15	21,000 + 45 MWe	Selexol™	3.6 – EOR
Beluga, Alaska, USA		80,000 + 300 MWe	Possibly Selexol™	
Rentech, Natchez, Mississippi, USA	Cancelled?	25,000	na	
SCS Energy New Jersey, USA	Cancelled?	? + 400 MWe	na	5.0
Freedom Energy Diesel, Tennessee, USA			na	
Adams County, Mississippi, USA	Post 2012	10,000	na	
NRG, Fox Creek, Alberta, Canada	Post 2014	40,000	na	EOR
Strike Oil FutureGas, Otway Basin, Australia	2016	10,000 + 40 MWe	na	
Altona Energy/CNOOC, Arckaringa Basin, Australia		30,000 + 560 MWe	na	
Shenhua Group, Ordos City, Inner Mongolia	Phase I: 2011 Phase II: tbd	1 Mt/y crude oil 2 Mt/y crude oil	90% capture 90% capture	Phase I 100 kt/y Phase II >1 Mt/y

to a demonstration plant where it is injected at a pressure of 35–40 MPa into a deep saline aquifer. Injection commenced in January 2011 and is expected to continue until 2014. In August 2012, it was announced that during the preceding 15 months, the project had captured successfully 40 ktCO₂. It is expected that by June 2014, 300 kt will have been stored in underground saline aquifers in the Ordos Basin; this has a capacity to store tens of billions of CO₂.

Shenhua is also undertaking a feasibility study into a second facility capable of handling 1 Mt/y of CO₂, and there are plans to possibly develop a larger facility capable of handling 3 Mt/y. Potential storage sites are being investigated for the second phase of the project (PEI, 2011). However, in both cases, no schedule for construction has been set. Announcements by Shenhua suggest that by 2015, the company will be producing 3 Mt/y of liquid products from coal. By 2020, potentially, capacity could have increased to 11 Mt of liquid products and 18.3 billion m³ of gas.

Various CTL projects are also proposed elsewhere (Table 6). Most have proposed the incorporation of some form of carbon capture system although in many cases, the precise nature has not yet been made public.

2.3.5 Future RD&D activities and challenges – pre-combustion capture

For coal-based power generation, IGCC technology is considered to one of the cleanest and most efficient options. Current plants are considered to be at TRL-8. Although only a small number of plants are currently operational, there are a number of important IGCC + CCS projects in the pipeline. For carbon capture, pre-combustion capture using physical solvents is generally the technology of choice and as noted above, is being evaluated via a number of ongoing pilot-scale test programmes. With IGCC technology, there are multiple pathways of improvements using different gasification technologies that may find particular application more favourably with certain climatic conditions, geographical locations, and coal types (GCCSI, 2012c).

CO₂ separation using physical solvents has long been established in various industrial sectors, hence the technical feasibility of the process has been well proven. However, a number of avenues for improving various aspects of pre-combustion capture have been identified that would benefit from further RD&D efforts. In the case of coal-fuelled IGCC + CCS, a number of needs have been identified, many of which focus directly or indirectly on reducing the associated efficiency loss of the estimated 7–8 percentage points (GCCSI, 2012c).

Although incorporating carbon capture into an IGCC plant would increase overall capital costs, the biggest factor of the reduced economic performance is the loss of energy involved. Much current RD&D is aimed at reducing the energy losses encountered in the various steps of the capture and storage process. The largest and most damaging factor is the net power output loss. A major opportunity would be to scale-up processes that produce CO₂ at close to gasifier pressures, which would significantly reduce the parasitic power penalty. An example of such a process may be a chilled ammonia process adapted for pre-combustion capture (Oettinger, 2012c).

Some areas identified for further RD&D are more generic to IGCC technology in general (such as the development of larger high-firing temperature, high efficiency gas turbines) whereas others are more directly associated with the CCS technology; those highlighted include:

- improved availability of gasifier island;
- improved integration of air separation unit;
- improved supply of oxygen. The use of Ion Transport Membrane (ITM) technology could add ~1% to overall efficiency (*see* Section 9.1);
- development of improved solvents for physical absorption; higher CO₂ loading at a higher temperature, compared to existing solvents;
- development of novel methods for CO₂/H₂ separation (ceramic and polymer membranes);

- modification of gas turbines for efficient combustion of H₂-rich fuel (including prevention of NO_x formation) (VGB, 2004);
- modifying regeneration conditions to recover CO₂ at a higher pressure;
- improving selectivity to reduce H₂ losses;
- development of higher efficiency gas-liquid contactors;
- reducing regeneration energy requirements below that of commercially available solvents such as Selexol™ and Rectisol®;
- development of new types of sorbent. For instance, in the USA, a promising novel lithium silicate-based sorbent is being developed for high temperature CO₂ removal from syngas;
- further development of shift catalysts (performance, durability, cost reduction, admission of high CO concentration). Major catalyst suppliers have active programmes to improve catalyst performance so that they will operate at lower steam:CO ratios.

Around the world, several major research programmes are under way, examining how pre-combustion capture systems can be improved further. For instance, as part of its Carbon Sequestration Program, the US DOE/NETL is addressing a number of pre-combustion RD&D goals. It notes that current state-of-the-art pre-combustion technologies would increase the cost of electricity by ~30%. An overall programme goal is to identify technologies that will capture 90% of the CO₂ generated and limit the increase in cost to no more than 10%. Support is being provided for testing of the most promising technologies at pilot scale. Integrating NETL's existing portfolio of technologies with other advanced IGCC system improvements has the potential to reduce the added cost of pre-combustion capture from 30% to 16%. Recently, the DOE and EPRI have developed a roadmap for IGCC+ CCS technology that could potentially improve IGCC efficiency to a level that matches or exceeds that of the current IGCC technology without CO₂ capture.

The US programme is supporting a number of pre-combustion technology options that offer opportunities for significant cost reduction and/or improved performance. Several promising advanced technologies are being addressed. Examples of specific R&D efforts are shown in Table 7. Overall, numerous projects are under way involving range of R&D providers, academia and industrial partners.

Similarly, as part of the EU 7th Framework Programme, a range of multi-partner collaborative activities are under way in Europe. Research and demonstration activities in the field of clean coal technologies and CCS include ongoing examinations of advanced capture systems that include pre-combustion technologies. For instance, the DECARBit project (2008-12) is focused on the

Table 7 Examples of specific US pre-combustion capture R&D activities	
R&D area	Specific goals
Physical Solvents	<ul style="list-style-type: none"> – increase temperature and pressure operating window for solvent to reduce energy demand and compression requirements – reduce impacts of co-contaminants and temperature on solvent degradation – increase CO₂ selectivity
Solid Sorbents	<ul style="list-style-type: none"> – address pressure drop of CO₂ during flash recovery – reduce energy requirements needed to cool syngas for CO₂ capture and heating and re-humidify for firing to turbine – increase recovery of hydrogen during CO₂ capture
Membranes	<ul style="list-style-type: none"> – develop novel materials that will reduce material and manufacturing costs – examine impacts of co-contaminants, temperature, and pressure on membranes and solvents – improve selectivity to increase purity of CO₂ – improve permeability to decrease pressure drop

development of zero-emission pre-combustion power plants by 2020, with a capture cost of less than 15 €/t with the highest feasible capture rate. The project is covering different aspects of research, development and piloting of advanced candidate pre-combustion capture technologies. Work is proceeding via a series of work packages that are examining system integration and optimisation, advanced pre-combustion CO₂ separation, advanced oxygen separation technologies, enabling technologies for pre-combustion, coupled with pilot studies. It is anticipated that the project will help accelerate technology development and contribute to the deployment of large-scale CCS plants, in line with the adopted European policies for emission reductions. The DECARBit consortium involves 21 partners from ten countries.

3 Post-combustion capture

In post-combustion capture, CO₂ is removed after combustion of the fossil fuel (*see* Figure 6). Potentially, it can be separated from the other combustion species present in the flue gas and various ways of achieving high levels of CO₂ capture (such as chemical and physical absorption, adsorption, cryogenics and membranes) have been proposed or identified. However, some techniques are better suited to coal-derived flue gases than others (VGB, 2004). The main advantages and disadvantages of post-combustion capture are summarised in Table 8.

Globally, most coal-fired power plants (predominantly pulverised coal units) produce low pressure flue gas with a low CO₂ concentration (typically 10–15%). For many of these, carbon capture would most likely be based on some form of post-combustion solvent scrubbing, with separate solvent regeneration and recycle. Potentially, most such technologies are regarded as being suitable for deployment on both new-build power plants as well as for retrofitting to existing units.

Most of the major challenges outstanding for post-combustion capture revolve around the relatively large parasitic load that the CCS facility imposes on the power plant. Much of this results from the capture process, particularly the energy required to regenerate the solvent. Energy is also required for CO₂ compression, although this is less than that needed for capture; there is less potential for further significant saving in the area of compression. Globally, a significant proportion of RD&D activities are focused on finding ways to reduce the parasitic load imposed. Avenues being explored include the development of new chemistry, new process designs, and novel power plant integration schemes. Other important factors include reducing capital cost requirements, and minimising solvent volatility and degradation issues.

Post-combustion capture using solvents such as methanolamine (MEA) is commercially available and has long been used for various industrial applications. However, such capture processes were not designed specifically for application to large coal-fired power stations. Because of the large volume of flue gas to be processed, the necessary equipment is likely to be sizable and steam demand high. The presence of contaminants in the flue gas may also affect the efficiency of the capture process. Despite these issues, as it has the potential for retrofitting to many existing coal-fired power plants, post-combustion capture is viewed as having the greatest near-term potential for reducing CO₂ emissions from the power sector. Many technology variants and options are being followed. For instance, a major RD&D programme is under way in the USA, examining both solvent and non-solvent based post-combustion capture (Table 9).

Currently, considerable development is taking place around the world with the emphasis on reducing costs and increasing process effectiveness, and a number of technology variants are being pursued. However, alongside technical barriers to be surmounted, there are a number of non-technical hurdles that need addressing before such capture systems become deployed widely. Several are universal and apply to all types of CO₂ capture process (IEA, 2006). They include:

- cost – demonstration of commercial operation and safe permanent storage. CCS investment poses a major financing challenge. Governments need to establish credible, long-term policies to stimulate private investment;
- a regulatory framework (liability, licensing, royalties, leakage cap) is needed for private investment and public acceptance;
- emission mitigation mechanisms such as emission trading should include CCS;
- a substantial increase in the global RD&D budget and outreach to emerging countries are essential.

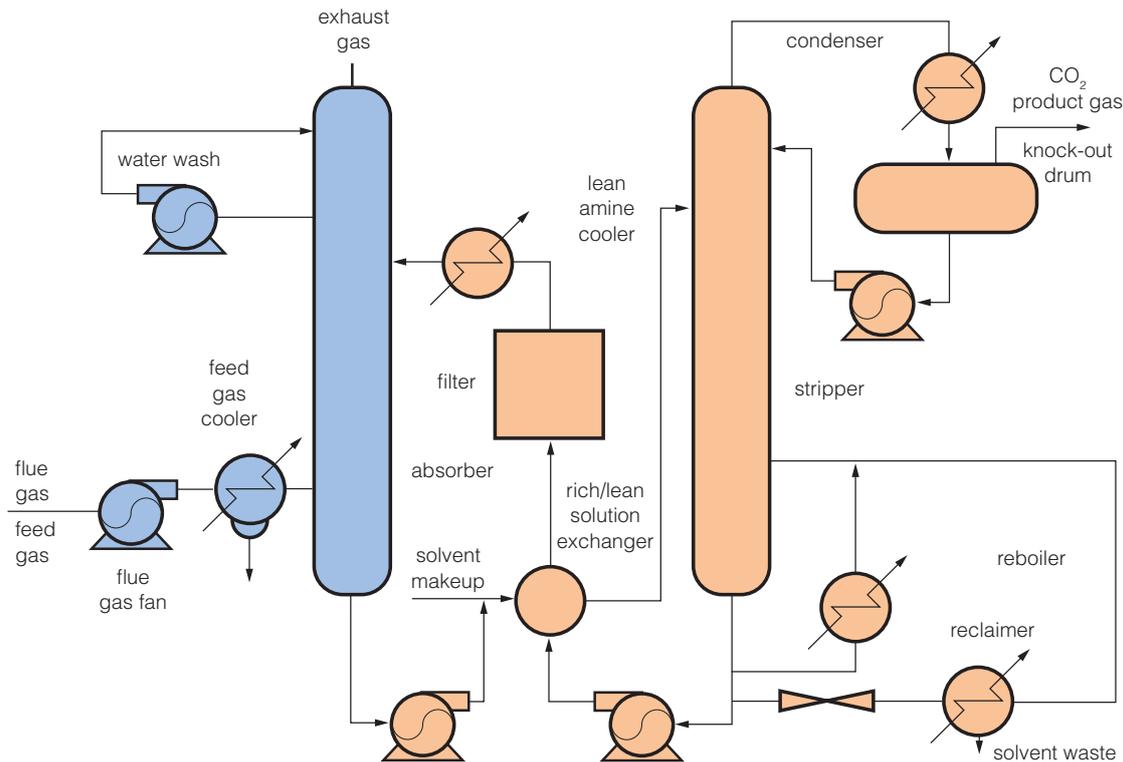


Figure 6 Process schematic for amine-based post-combustion CO₂ capture (IPCC, 2005)

Table 8 Advantages and disadvantages of post-combustion capture (Figueroa, 2008; GCCSI, 2012d; GCCSI, 2012e)	
Advantages	Challenges/barriers to implementation
Applicable to the majority of new and existing coal-fired power plants. Retrofit technology option	Flue gas is dilute in CO ₂ and at ambient pressure; low CO ₂ partial pressure
For both retrofit and new builds, enables the continued use of well-established pulverised coal technology, used worldwide	Amine-based processes are commercially available but at relatively small scale. Used mainly in non-power industrial applications. Considerable scaling up required
Extensive ongoing R&D to improve sorbents and capture equipment. This is leading to reduced energy penalty	Energy penalty – current amine technologies result in a loss of net power output of ~30% and a reduction of about 11% points in efficiency
Future improvements and developments of pulverised coal systems (such as USC materials) will increase plant efficiency and reduce CO ₂ emissions	Steam extraction for solvent regeneration reduces flow to LP turbine; this impacts on efficiency and turn-down capability
	Significantly higher performance or circulation volume required for high capture levels
	CO ₂ produced at low pressure compared to storage requirements
	Most sorbents need very pure flue gas to minimise sorbent usage and cost
	Considerable water requirement – nearly double per net MWh for water-cooled plants

Table 9 US Department of Energy's post-combustion CO₂ capture RD&D programme (Ciferno, 2010)		
Solvent development		
Solvent R&D focus: <ul style="list-style-type: none"> – high CO₂ working capacity – optimal regeneration energy – low heat capacity – fast kinetics – thermally and chemically stable – non-corrosive, environmentally safe 		Technology status 2010: laboratory scale 2011: 2.5 MWe pilot (Siemens) 2015: 5–25 MWe pilot scale 2018: demonstration scale
R&D partners University of Notre Dame, Ion Engineering, Siemens Energy, Georgia Tech, Illinois St. Geological Survey, 3H, GE Research Corporation, Lawrence Berkeley Nat. Lab, NETL Office of R&D		
Development activities		
Use of potassium carbonate as solvent (with carbonic anhydrase enzymes as reaction accelerators)	Illinois State Geological Survey	Currently laboratory scale
R&D focus: Enzyme durability, cost, process design, vacuum stripping		
CO₂ capture by self-concentrating amine absorbent	3H Company Inc	Currently laboratory scale
R&D focus: Development of solvent/absorbent mixtures that can separate into two phases upon CO ₂ absorption – only regenerate the CO ₂ -rich phase		
Siemens POSTCAP amino acid CO₂ capture technology (see Section 4)	Siemens Energy Inc	5000 hours bench scale 2.5 MWe amino acid solvent slipstream at TECO's Big Bend Station
Other developments (non-solvent-based)		
Advanced CO₂ sorbent development	UOP University of Akron ADA-ES SRI International TDA NETL Office of R&D	2011: 1 MWe pilot scale 2016: 5–25 MWe pilot scale 2020: demonstration scale
R&D focus: <ul style="list-style-type: none"> – high CO₂ working capacity – fast reaction kinetics – durability: thermal, chemical, mechanical – gas/solid systems – low pressure drop, heat management 		
Solid Sorbents: Pilot-scale development	ADA-ES Inc	1 kW pilot-scale slipstream tests began in Jan 2010 at three field sites in the USA
R&D focus: <ul style="list-style-type: none"> – evaluate performance of >100 CO₂ capture sorbents at bench-scale using simulated flue gas – assess working capacity, reaction energy, theoretical regeneration energy, consistent performance, reaction kinetics, durability, cost 		
Advanced flue gas CO₂ membranes	Membrane Technology Research RTI International Air Liquide Gas Technology Institute	2010: 1 t/d slipstream (MTR) 2011: 1 MWe pilot scale 2015: 5–25 MWe pilot scale 2018: demonstration scale
R&D focus: Building on existing technology at similar scale (NG purification)		
Hybrid Membrane/Absorption Process (Membrane Contactor)	Gas Technology Institute PoroGen Corp Aker Process Systems	Planned slipstream test at Midwest Generation's Joliet Power Station (25 kWe)

3.1 Current post-combustion capture technology status

Extensive reviews examining the current position regarding technology development and status have been undertaken by organisations such as the IEA, GCCSI, the US DOE and EPRI. These have confirmed that a significant proportion of ongoing activities are focused firmly on reducing the costs and minimising the energy penalties of the various capture systems.

Although in recent years, the level of activity in the field of post-combustion capture has increased substantially, some systems are viewed as still being at relatively early stages of development. Based on the assessment system described in the Appendix, most current technologies fall between *Technology Readiness Levels* (TRLs) of 1 and 5; this corresponds to the conceptual design and laboratory-bench scale categories. Only a small number of projects are ranked at TRL-6, corresponding to the pilot plant stage. The studies undertaken show that most of the new processes under development employ absorption methods (solvents) for post-combustion CO₂ capture. Fewer new processes and concepts utilise membranes or solid sorbents (adsorption), a reflection of the greater challenges facing those approaches (Folger, 2010).

However, development in these fields is being pursued by various organisations. For instance, in the USA, ADA-ES is building a 1 MW pilot capture plant based on the use of its own regenerable solid-sorbent. This is being installed at Alabama Power's coal-fired Miller Electric Generating Plant near Birmingham, Alabama. The plant is scheduled to commence operation in October 2013. It is claimed that the technology offers the potential to reduce significantly the energy penalty associated with CO₂ capture. Results from pilot testing will be used to develop a preliminary full-scale commercial design in preparation for demonstration at the next scale. ADA is the prime contractor for this US\$20.5 million project that is being administered by NETL. This is providing US\$15 million of the funding through the American Recovery and Reinvestment Act. Southern Company is co-funding the project with other participants.

3.1.1 Amine-based post-combustion capture systems

Amine-based absorption systems were developed over 60 years ago, primarily to remove acid gas impurities such as H₂S and CO₂ from natural gas streams. Later, the process was adapted to capture CO₂ from flue gas streams for subsequent use in chemical manufacture, food and beverage production, and enhanced oil recovery. The use of amine-based solvent scrubbing processes has been examined in detail by, for instance, Davidson (2007). Process operations and individual amines (simple and hindered amines, and solvent blends) available and their respective advantages and disadvantages was discussed. Globally, there are more than 2000 coal-fired power plants in operation. It is considered widely that one of the most attractive options for controlling CO₂ emissions from these would be to retrofit as many as possible with carbon capture systems. At present, the lead contender for this would appear to be solvent scrubbing using amine-based solvents.

Amines react with CO₂ to form water soluble compounds and are therefore able to capture CO₂ from streams with a low CO₂ partial pressure, although capacity is equilibrium-limited. Thus, amine-based systems are potentially suitable for application to flue gas of conventional pulverised coal-fired power plants. Such technologies are expected to be the front runners for large-scale application to such plants. However, traditional CO₂ capture processes utilising conventional amine solvents are energy intensive and the solvents are susceptible to degradation by oxygen, SO_x and NO₂ present in coal-derived flue gas; invariably, this increases plant operating costs. A key feature of the system is the large amount of heat required to regenerate the solvent (normally at ~120°C). Usually, most schemes propose extracting the heat required from the steam cycle, reducing the net efficiency of the power plant. There may also be issues of corrosion and as a result, uninhibited MEA is generally limited to about 15–20wt% concentration. However, the water is a diluent and this places additional demands on the process sizing and energy requirements. This low concentration raises the reboiler duty

Table 10 Advantages and disadvantages of amine scrubbing (Jones, 2007; VGB, 2004; Susta and Luby, 2007; Davidson, 2007; Marano and others, 2011)	
Advantages	Disadvantages
Well established in different industries (>50 years) Can be retrofitted to some existing power plants in suitable locations Has been proven on a few small scale coal-fired power plants	Need to treat large volumes of flue gas with limited CO ₂ content
Applicable to low-CO ₂ partial pressures	Process consumes considerable energy. Little point in retrofitting power plants of low thermal efficiency since the efficiency losses would render the plant uneconomic
MEA commonly used; solvents are inexpensive	Relatively low boiling point of MEA may result in solvent carryover into the CO ₂ removal and regeneration steps
Recovery rates of up to 98% can be achieved	Presence of oxygen in the flue gas can increase corrosion and solvent degradation in the absorption system Uninhibited alkanolamines such as MEA and DEA can be oxidised to give carboxylic acids and heat-stable amine salts
Product purity >99% vol% can be achieved	Concentrations of CO ₂ and NO _x in the gas stream combine with the amine to form non-regenerable heat-stable salts
May offer flexibility if system can be switched between capture and no capture	Hot flue gases cause solvent degradation and decrease absorber efficiency. Inlet flue gas limit of 50°C for MEA based solvents
Amines offer potential cost reductions if the technology proves to be analogous to other technologies	SO _x in the flue gas reacts irreversibly with MEA-based solvents to produce non-reclaimable corrosive salts
There is a strong research base that should lead to improved solvents and processes	Because of its high reactivity, MEA can react with carbon oxysulphide (COS) and carbon disulphide (CS ₂), degrading the solvent
	Fly ash in the absorption solvent may cause foaming in the absorber and stripper, scaling and plugging of equipment, erosion, corrosion and increased solvent loss through chemical degradation and physical association with the waste sludge

substantially, although by applying inhibitors, amine concentration can be increased to ~25–30 %, thus reducing the heat demand. The main advantages and disadvantages of amine scrubbing are summarised in Table 10.

Essentially, amines for CO₂ capture are available in three forms (primary, secondary and tertiary) each with its advantages and disadvantages as a CO₂ solvent (Davidson, 2007). The most commonly encountered primary amine is MEA. Secondary amines include diethanolamine (DEA) and diisopropylamine (DIPA). Secondary amines have lower capture reaction heat and have some advantages over primary amines. For example, the reaction heat of CO₂ with DEA is 1.5 MJ/kg, compared with 1.9 MJ/kg for primary amines. This makes the use of secondary amines more economical in the regeneration step than using MEA. However, secondary amines share the other downsides of primary amines. Tertiary amines such as triethanolamine (TEA) and methyl-diethanolamine (MDEA) are even less reactive. They require the least heat to liberate the CO₂

from the solvent. For example, MDE's capture reaction heat is just 1.3 MJ/kg (Susta and Luby, 2007). Because tertiary amines react more slowly with CO₂, they must be circulated more quickly than primary and secondary amines. However, tertiary amines degrade and corrode more slowly than primary and secondary amines.

In addition to options for the type of amine, solvent blends may be utilised or additives used to enhance system performance. Increasing the amine concentration through the addition of corrosion inhibitors and advanced formulations is therefore a high priority for the manufacturers of commercial systems.

3.2 Commercially available capture systems

There are a number of technologies available that can be considered as potential candidates for large-scale application to coal-fired power plants. Most use either aqueous pure amines or blends of amines. Most commercially available systems are generally based on the use of amines such as MEA, MDEA or so-called advanced 'designer' amines (Herzog and others, 2009). In terms of technology maturity, post-combustion capture technologies applied to coal-fired power plants are considered to be at TRLs of up to 7 (at pilot plant scale, >5% of commercial scale), the same level as oxyfuel combustion. In contrast, pre-combustion systems are considered to be higher at TRL levels of up to 9 (full-scale commercial deployment) (GCCSI, 2011).

The main technology vendors are noted below. Where information has been made available, RD&D, technology developments and research proposals are discussed. However, in some cases, issues of commercial confidentiality have limited the extent and scope of information made available in the public domain.

3.2.1 ABB/Lummus and Alstom/Dow Chemical

During the 1970s, Kerr-McGee developed a system used primarily to capture CO₂ from coal-fired boilers (for EOR purposes) using a 15–20% MEA solution without an inhibitor. In 1990, the technology was licensed by ABB/Lummus, the company gaining worldwide exclusive marketing rights and becoming responsible for marketing and basic engineering. The technology is capable of capturing >96% of CO₂ from flue gases, but the lower sorbent concentration leads to economic disadvantages in terms of greater capital requirements due to larger equipment size and higher energy requirements compared to some competing newer technologies. However, the system is used commercially on several coal-fired power plants and industrial facilities. In 2009, Alstom acquired the Lummus Global engineering unit, becoming Alstom Carbon Capture GmbH; this was integrated into Alstom's CO₂ Capture Systems activity.

Alstom has had commercial links with the Dow Chemical Company for some years. Under the terms of their arrangement, Alstom focuses on improving the capture process and advancing plant integration. Dow, the world's largest supplier of amines, maintains its own RD&D programme aimed at further solvent development. This has included a test programme on a pilot capture facility (TRL-7) fitted to a coal-fired boiler in South Charleston, West Virginia, USA. This used proprietary *Advanced Amine Process* (AAP) technology (with Dow UCARSOL FGC 3000 solvents) developed jointly by Alstom and Dow under their joint development agreement. The pilot plant operated for >5000 hours (until November 2011) and captured ~90% of the CO₂ present in the flue gas (Klinkera and others, 2011).

Projects

Several larger demonstration projects are proposed. At EDF's 600 MW coal-fired **Le Havre power plant** in France, Alstom is to develop, construct, operate and test a 25 tCO₂/d capture facility (TRL-6)

using the Advanced Amine Process. The capture facility will be fed by a flue gas slipstream from the power plant. It is anticipated that a one-year test programme will help verify the optimised performance of the technology, particularly with regard to energy consumption and operational flexibility within an industrial setting. No CO₂ storage is proposed. The project is scheduled for start-up by 2012.



Figure 7 The Belchatów power station in Poland (photograph courtesy of PGE)

A second major ('technology validation') programme is planned for the coal-fired **Belchatów power plant** in Poland operated by PGE Elektrownia Belchatów (Figure 7). The station is Europe's largest individual CO₂ producer (>30 Mt/y). During Phase I of the programme, a pilot CCS facility will treat a proportion of the flue gas from the existing Unit 12, capturing around 0.1 MtCO₂/y (TRL-7). This is scheduled to be operational by 2014.

Phase II will comprise a larger demonstration project and will be based on a new 858 MW supercritical PCC unit currently under construction. The capture plant will treat a portion of the unit's flue gas (equivalent of 260 MWe) (TRL-8) and is expected to be operational by 2015. CO₂ capture rate will be 90% and around 1.8 MtCO₂/y will be captured (~235 t/h) for storage in a saline aquifer. The heat consumption of the carbon capture plant will be 2.2 GJ/t of CO₂ and energy consumption will be around 40 MWe. It is anticipated that the new supercritical power unit will have an efficiency without carbon capture of around 41.7%. With the capture plant operating (with vapour to amine regeneration, but without CCS equipment

demands) this will fall to ~39.8% (Wdowiak, 2010). Captured CO₂ will be compressed and piped to a suitable deep saline aquifer within 60–140 km of the power plant. Three possible storage sites are under consideration (Budziszewice, Lutomiersk-Tuszyn, and Wojszyce).

Main project partners comprise Alstom and Dow Chemical (capture technology and solvent), Gazoprojekt (CO₂ transport feasibility study), the Polish Geological Institute (PIG) and Schlumberger (support during first appraisal phase). Other subcontractors include PBG Ltd, Geofizyka Toru Sp z o.o, and PRWiG. The project is being supported by the European Commission with a €180 million allocation from the European Energy Programme for Recovery. The schedule (as of late 2011) for the CCS plant is shown in Table 11. However, in May 2012, PGE announced that the company was in 'no position to proceed with the project' without the addition of state support or other incentives. PGE considers that without such support, the project would be unprofitable. Therefore, the current status of the project remains unclear.

Planned RD&D activities

Alstom and Dow Chemical plan to continue their efforts to improve solvent properties and capture process efficiency. Alstom is developing enhanced plant integration schemes. A major area in the development of the Advanced Amine Process is to quantify and maximise the amount of savings, both in capital expenditure and energy requirements, relative to conventional amines. Dow Chemical is maintaining its R&D activities aimed at further solvent development. As part of this, the pilot plant

Table 11 Development schedule for the Belchatów power plant CCS project (Wdowiak, 2010)		
Task	Planned timescale	Current status
Capture installation		
Building permit validation	February 2010 – completed	Modification to unit's flue gas system and main cooling water system (capture ready) completed
Completion of capture-ready modifications/mechanical completion	June 2010 – partially completed Mechanical completion due by December 2013 - to be confirmed following selection of CCP contractor	
		FEED study – 90% completed Contracting structure of capture plant – nearing completion Design and construction of pipeline steam extraction – under order
CO ₂ transport		
Building permit	August 2013	
Construction completion	November 2014	
Transport feasibility study		Feasibility study completed – three possible routes included in Lodz Voivodeship Zoning Master Plan
Permitting		Preparatory permitting activities will start ASAP
Contractor selection		Turnkey contractor will be selected after storage site selection
Storage		
Storage site selection	First half of 2011	2D seismic work, drilling tests, gravimetric and non-conventional research performed within area of two structures (2000 km ²) Modelling and site selection in 2011 followed by further development of storage component via selected site characterisation and storage site localisation
Permit application and storage site construction start-up	December 2012	
Construction completion	December 2014	
Injection permit	December 2014	
Optimisation process completion and CCS final acceptance	December 2015	

development programme in West Virginia using the Advanced Amine Process technology with Dow's UCARSOLTM FGC-3000 advanced amine solvent is continuing. Other areas will be explored as part of the activities under way at Belchatów.

3.2.2 Fluor Econamine FG+

During the 1970s, Dow Chemical developed a system based on a 30% MEA solution. This was intended primarily for use on natural gas plants. In 1989, the technology (Econamine FG) was acquired by Fluor Daniel Inc Worldwide, Fluor now has licences for 27 plants equipped with its proprietary technology, operating on a range of flue gas sources that include steam reformers, gas engines and turbines, and natural gas fired boilers. In the case of the latter, the system has demonstrated >95% availability, specifically on a 350 tCO₂/d capture plant in Bellingham, Massachusetts (although the unit was closed down in 2005 when the host power plant was converted from base load to peaking operation). However, it remains the only unit in the world with long-term operating experience with a gas turbine exhaust, (Reddy, 2011).

The current Econamine FG+ technology is regarded widely as the state-of-the-art commercial baseline, with which to compare other CO₂ capture technologies. The system is well proven and has a significant operating history at commercial facilities, capturing CO₂ from multiple sources that include low CO₂ concentration flue gas (<3% vol) with high oxygen concentrations (up to 15% vol). The solvent is based on MEA (30%wt solution) with an inhibitor to resist carbon steel corrosion; it is inexpensive and readily available.

Fluor offers a number of options that allows systems to be tailored to meet specific requirements. These include enhanced solvent formulations, lean vapour compression configurations, low emissions configurations, advanced reclaiming technologies, and absorber intercooling. The use of the latter allows greater flue gas CO₂ concentrations that lead to higher operating temperatures; this generates faster reaction kinetics and improved solvent carrying capacity (Reddy, 2011) and helps lower solvent recirculation rate, reduce steam consumption, and reduce capital costs for recirculation equipment. Advanced reclaiming systems now offered can help minimise high temperature solvent degradation and residence time. Fluor has also developed a new low temperature, low residence time reclaiming process capable of removing both heat stable salts and degradation products. Several commercial plants have also adopted the use of a higher solvent concentration which has allowed reduced energy consumption, reduced amine recirculation rate, and lower capital costs. Processes with very low regeneration temperatures (~70-90°C) allow the use of modified steam cycle configurations with back pressure turbines; this helps minimise power reduction and efficiency losses (Ploumen, 2012).

Projects

The basic Econamine FG+ technology has been demonstrated on a coal-fired power plant belonging to Tokyo Electric Power (TEPCO) in Kawasaki, Japan. Here, a pilot plant captured successfully 5 tCO₂/d (TRL-6)

More recently, a project was developed for E.ON's coal-fired power plant in **Wilhelmshaven** in Germany where a 5.5 MW pilot plant (TRL-7) was retrofitted to the plant. It treats 20,000 m³/h of flue gas and recovers 3 tCO₂/h (Radgen, 2011). Operations began in September 2011.

The use of Econamine FG+ technology is planned for the proposed *ROAD* CCS demonstration project (Rotterdam Opslag and Afdwang Demonstratieproject - Rotterdam Capture and Storage Demonstration Project), a joint venture (the limited partnership Maasvlakte CCS Project C.V) between E.ON Benelux and Electrabel Netherlands (now GDF Suez Energy Netherlands). This is to be located at the 1100 MW coal-fired **Maasvlakte (MPP 3) power plant** in The Netherlands and will involve the capture of CO₂ from the plant's flue gas (equivalent to 250 MWe) (TRL-8) using Fluor's technology. Fluor is also providing EPC services to the project (Reddy, 2011). It is anticipated that ~1.1 MtCO₂/y will be captured from the plant; a total of 5 Mt will be captured over the demonstration phase of the project. Following compression, cooling, dehydration and metering, this will be transported via a 25 km pipeline for injection into a depleted offshore gas field (Rode and Meyer, 2011; Radgen, 2011).

Major milestones in the development of the ROAD project include:

- September 2009 – project selected for funding by European Commission;
- May 2010 – Ministerial order for Dutch funding published. Grant Agreement signed by European Commission and ROAD;
- September 2010 – FEED studies for capture plant completed;
- 2nd quarter 2012 – final investment decision;
- 2012 – start of execution phase (procurement, construction, etc);
- 2014 – mechanical completion of CCS chain;
- 2015 – start of operation of CCS chain;
- 2015-19 – demonstration/operation phase of CCS chain;
- 2020 – start of commercial operation of CCS chain.

The ROAD project is being co-financed by the Government of the Netherlands, the European Commission within the framework of the European Energy Programme for Recovery (EEPR) and the Global CCS Institute.

A demonstration project is planned for a 60 MW equivalent slipstream (TRL-7) project on the 600 MW Unit 7 at NRG Energy's **WA Parish Plant** in Sugar Land, Texas, USA – the *WA Parish Post-Combustion CO₂ Capture and Sequestration (PCCS) Project*. Each of the plant's four coal-fired units consume ~36 kt/d of PRB coal. The main goals are for the project to:

- demonstrate the applicability and impacts of post-combustion CCS on a commercial coal-fired plant;
- demonstrate the use of anthropogenic CO₂ for EOR applications;
- demonstrate protocols for monitoring, verification, and accounting (MVA) of CO₂;
- identify concepts that will improve economics and/or efficiencies in order to progress toward DOE's goal of achieving a maximum of a 35% increase in the cost of electricity generated (Stopek and others, 2011).

The project is being taken forward by means of a three-phase programme. Phase 1 has been completed and consisted of project definition/FEED. Phase 2 will cover detailed EPC, and Phase 3 will focus on demonstration and monitoring activities. Around 1200 t/d of CO₂ will be captured and used for EOR. A CO₂ capture rate of 90% is envisaged. The FEED study for the plant was undertaken between 2010 and 2011. Construction was expected to begin in 2013, with commissioning starting in July 2014. A two-year test programme was planned (Fluor, 2010). However, this may now change. The original development plan for the WA Parish station was for a slipstream unit on Unit 7. This unit has no FGD. However, the possibility of increasing the project to a 240 MW equivalent scale is currently being assessed. This would be based on the 650 MW Unit 8; this incorporates an FGD plant, low NO_x burners and an SCR unit. At the proposed scale, the capture plant would recover 90% or more of the CO₂ from the unit's flue gas (~4770 t/d). At this scale, the viability for use in EOR would be increased greatly. Current thinking is that the 60 MW plant would generate ~400 ktCO₂/y, insufficient for meaningful EOR application. The proposed 240 MW-scale project would produce 1.6 Mt/y – this is considered economically viable. Preliminary designs/FEED for the 240 MW plant are expected early in 2012 (Stopek and others, 2011).

Other recent US proposals include the 765 MW coal-fired supercritical PCC **Tenaska Trailblazer Energy Center** near Sweetwater in Texas. The project is expected to be the first new-build coal-fired power plant in the USA to incorporate a post-combustion carbon capture plant into the initial design. The plant will fire low sulphur PRB coal and is due to begin commercial operation in 2015-16. After bid evaluation, Tenaska selected Fluor to license, engineer, procure, and construct the capture plant based on its Econamine FG+ technology. Some 85–90% capture is envisaged, amounting to ~16.5 kt/d (Christensen and Dysert, 2012) or 5.75 Mt/y (TRL-9). CO₂ from the project will be sold into the Permian Basin CO₂ market, where it will be used for enhanced oil recovery.

In Italy, ENEL (with ENI) set up a pilot-scale (2.5 tCO₂/h) (TRL-6) post-combustion capture facility

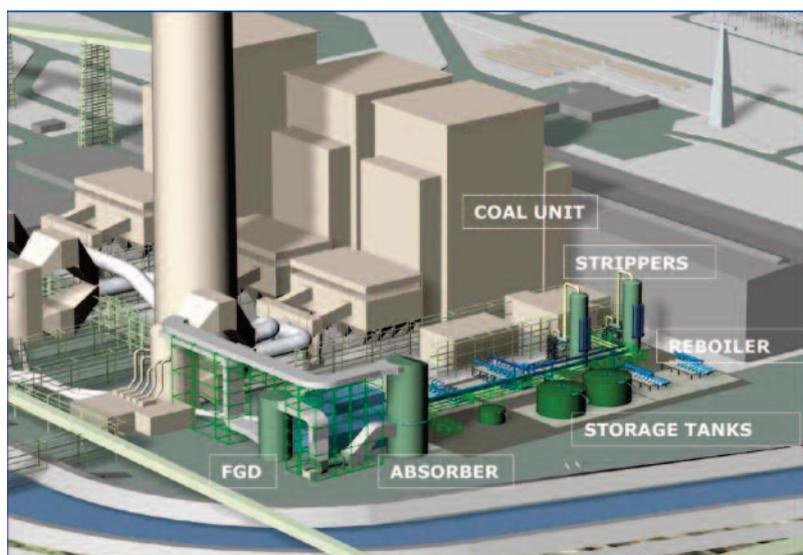


Figure 8 Schematic of ENEL's CO₂ capture plant at Brindisi
(photograph courtesy of ENEL)

at the **Federico II power plant** at Brindisi (see Figure 8). By the end of 2011, this had achieved ~2500 hours of operation, capturing more than 5 ktCO₂ that was injected at the ENI/Stogit site in Cortemaggiore. Useful data and operational experience under different conditions was achieved using MEA and advanced solvents with various inhibitors. Further solvent and inhibitor testing is planned with the aim of reducing power consumption, limiting solvent degradation and improving environmental performance (Benelli, 2011). The overall intention of the programme is

to acquire useful know-how on the design of future larger scale applications of CCS. It was intended that the first industrial-scale application of the technology was to be at ENEL's Porto Tolle power plant. This was to be converted from oil-firing to supercritical coal-fired operation. However, in May 2011, the authorities revoked permission for the conversion. The demonstration plant proposed for the site would have used Econamine FG+ technology to treat 810,000 m³/h of flue gas (40% of output from one of three 660 MW units proposed) capturing ~1 MtCO₂/y. This was to be stored in a saline aquifer deep below the Adriatic Sea. The future of the project is now uncertain. It is currently described as being 'on hold'.

In a separate development, a collaborative agreement was signed between the Chinese Ministry of Science and Technology, the Italian Ministries of the Environment and Economic Development, and ENEL. The latter is now co-operating with China-Huaneng on the design and development of a carbon capture system for the (sub-critical) 637 MWe **Tongchuan power plant** in Shaanxi, China. Captured CO₂ will be used for EOR. Phase I of the project is centred on a pre-feasibility study. Future plans for the station include the possibility of adding two 1000 MW supercritical PCC units (Benelli, 2011).

In 2010, Fluor formed an alliance with Babcock & Wilcox Power Generation Group to market and sell carbon capture systems for existing coal-fired power plants in North America, with the main focus on the Econamine FG+ technology.

Planned RD&D activities

Many of Fluor's efforts are concentrated on minimising cost penalties associated with its Econamine FG+ technology and minimising solvent losses. Its ongoing efforts in recent years have so far reduced steam and power requirements by 25–30%. It is considered that there are still significant opportunities for further reductions in the total costs of large Econamine FG plants, and Fluor is undertaking various engineering studies on units in this size range. It is suggested that by suitably scaling up the technology, the capital cost of a single train size plant (for a 4600 t/d coal-fired plant) could be reduced on a per tonne basis by between 47% and 54%. Various process options and configurations are being examined. For instance, if the CO₂ recovery unit used steam extracted from the low pressure steam turbine to reboil the stripper, and preheated boiler feedwater using the stripper overhead cooler, the steam demand of the CO₂ recovery unit could be reduced significantly.

Good hydraulic performance of vapour and liquid in columns is critical for successful plant operation.

As part of its efforts to scale up its technology, Fluor is continuing to develop enhanced absorber columns. To date, CFD studies have been completed and practical testing of liquid distributors is planned (Reddy, 2011). Special packing allowing a large contact area between flue gas and solvent with a low pressure drop over the column will allow reduced energy consumption by the fan (Ploumen, 2012).

Pilot plant investigations will also continue at the WA Parish power station in the USA. During the course of the project, a number of technology improvements will be evaluated. These will include absorber intercooling, lean vapour flash/compression, an improved solvent reclaiming system, testing of new solvents, an integrated SO_x trim removal/gas conditioning system, and demonstration of an integrated gas turbine (Reddy, 2011). Phase 3 of the ongoing programme will focus on a range of system demonstration and monitoring activities. This will encompass demonstration of the technology's specific advanced features and the CO₂ capture process, and the testing of novel solvents; this will include a piperazine-based solvent developed by the University of Texas. Other activities will examine the use of CO₂ for EOR purposes, and associated MVA requirements. CO₂ compression using Ramgen compression technology will also be evaluated.

3.2.3 Kansai Electric Power Company (KEPCO)/MHI KM-CDR process

For some years, Kansai Electric Power Company and Mitsubishi Heavy Industries (MHI) of Japan have been developing a process named KM-CDR based on proprietary sterically-hindered amine-based solvents (the KS series). These are claimed to require a lower circulation rate due to higher CO₂ loading capabilities, and have a lower regeneration temperature, lower heat of reaction, lower solvent degradation, and lower rate of corrosion compared to other amine-based processes. MHI recently improved its process and, following testing on its Nanko pilot plant in Japan, claims that the energy requirements of CO₂ capture and regeneration have been reduced to 2.53 MJ/kg using KS-1 solvent, and 2.44 MJ/kg for a new solvent. These advances should help to further reduce overall operating costs. The process is claimed to be the most energy efficient of the commercial offerings and has been applied to a number of industrial applications (KS-1 was first commercialised in a urea production application).

A development programme, focused around a 1 tCO₂/d pilot plant (TRL-5) was undertaken at MHI's Hiroshima R&D centre. This aimed to demonstrate CO₂ capture from coal-fired flue gas using KS-1 solvent. A series of tests was carried out investigating the impact and treatment of different impurities. A number of different coals were tested. The purity of the CO₂ stream produced was ~99.8% (dry) (Davidson, 2007).



Figure 9 Alabama Power's coal-fired Plant Barry power station, near Mobile, USA (photograph courtesy of Alabama Power/Southern Company)

Projects

Between 2006 and 2008, the MHI process was demonstrated successfully using KS-1 solvent at a scale of 10 t/d CO₂ capture from coal-fired flue gas at Georgia Power's **Yates Power Plant** in the USA. The project generated specific technical data on impacts of flue gas impurities and the adoption and deployment of measures to counter some of these. It also provided useful data for scaling-up the process which was applied to a larger 25 MWe unit (TRL-7) that began operation in June 2011 at Alabama Power's 2.66 GW coal-fired **Plant Barry power station**, near Mobile (see Figure 9). This is being operated on a slipstream from the seven-unit plant and has a capture capability of ~150 ktCO₂/y (~500 t/d).

The CO₂ captured is being supplied to the Southeast Regional Carbon Sequestration Partnership (SECARB) for transport by pipeline and injection into an underground site within the Citronelle oil field. This project will demonstrate end-to-end CCS from a coal-fired power station.

Planned RD&D activities

In the near term, the main focus of the RD&D programme will be on Alabama Power's coal-fired Plant Barry station in the USA. A major goal of the capture programme will be to enhance capture operations through the development of improvements to waste heat integration with the solvent system. Modelling suggests that a fully heat integrated high-efficiency system will improve by 26% (compared to an un-integrated case) the thermal energy performance of an integrated capture and power plant. Originally, it had been planned to install a 160 MW slipstream project at Plant Barry, capable of capturing around 1 MtCO₂/y of. However, for economic and other reasons, the decision was made not to move forward with this larger project at this time.

KEPCO and MHI plan to continue with the development of new, higher performance solvents and processes aimed at reducing associated energy requirements. This will be an important step in increasing the attractiveness of the technology for large-scale commercial deployment. Should the ongoing R&D programme produce solvents with improved properties, these may supplant existing commercial offerings (Tatsumi and others, 2009). In addition to the development of new absorbents, KEPCO and MHI have been evaluating vapour-liquid equilibrium and reaction kinetics for a range of newly developed absorbents – this work will also continue. Based on successful pilot plant programmes, associated costs have already been reduced. For instance, recent process improvements have reduced steam requirements by more than 10% below that required previously for the conventional MHI process using KS-1; efforts will continue to reduce this further.

Alongside the development of improved solvents, the main focus will be on reducing process costs through the application of improved process configurations. As part of its efforts to reduce costs, a novel heat integration system that forms part of the CO₂ regeneration process has recently been patented.

Successful pilot-scale operations mean that there is now a major emphasis on application of the technology in commercial-scale CO₂ capture plants. Data is being collected on flue gas characteristics from different types of coal-fired CCS demonstrations around the world. This is being used to tailor the Kansai/MHI process, helping to minimise process operating costs. Any future capture plants are expected to benefit from recent process improvements as well as those still being developed.

MHI's ongoing R&D programme is addressing a number of process characteristics. A particular focus is the influence of impurities and minor constituents present in coal-fired flue gas on capture performance and long-term stable, reliable operation. Since 2006 MHI has been conducting long-term CO₂ recovery verification tests at J-Power's **Matsushima power plant**. Here, a 10 t/d plant (TRL-6) using KS-1 solvent is capturing CO₂ from plant flue gas containing 14% (vol) CO₂ (Iijima and others, 2011). For some time, MHI has been examining the accumulation of impurities in the capture plant and evaluating the influence of minor flue gas components on KS-1. Results are helping to reduce technical risk associated with the scaling up of the process.

An important part of MHI's development programme is the further development and commercialisation of the company's *Zero Amine Emission* technology (see Section 3.4.2).

3.2.4 HTC Pureenergy

HTC Pureenergy offers a process package based around a CCS plant of pre-engineered modular design that is claimed to be suitable for capturing CO₂ from various industrial sources. A mixed amine solvent is used. The basic design incorporates a flue gas conditioning unit, CO₂ absorption system,

and a solvent recovery system. Modules are added downstream from the capture plant to handle CO₂ compression and dehydration, ready for transmission of the captured CO₂. The current package allows capture of up to 1000 tCO₂/d although developments are in hand to scale this up to 3000 t/d.

Specialised amine solvents (*Regina Solvents* – RS) are offered. These are a family of proprietary designer solvents developed at the International Test Center for CO₂ Capture (ITC) in conjunction with the University of Regina, Canada. They can be formulated for enhanced absorption and loading characteristics, improved stripping and stability, while minimising corrosion. This allows the provision of optimised separation of CO₂ from different types of flue gas stream.

Thermal-Kinetics Optimization (TKO) is an amine-based capture plant process configuration patented by ITC aimed at minimising CO₂ capture energy requirements. The combination of RS and TKO is claimed to reduce heat and energy requirements, thereby reducing the parasitic load on the emitter, and hence, the overall cost of operation.

Projects

In the UK, Doosan Power Systems have been responsible for the design, construction and commissioning of a 5 MWe pilot plant (CCPilot100+) (TRL-6) using advanced amine scrubbing. This is located at the coal-fired **Ferrybridge power station** and is fed by a flue gas slipstream from the FGD-equipped Unit 4. The project is a collaboration between SSE, Doosan Babcock and Vattenfall, with funding from the Technology Strategy Board, DECC and Northern Way. Several UK universities are research partners. Doosan, UK Coal and Siemens provided FEED and construction services.

HTC Pureenergy process design technology has been integrated into the project and the company is working closely with Doosan. The plant employs HTC's Thermal Kinetics Optimization process, which aims to substantially reduce the energy requirements of capture. The baseline solvent at CCPilot100+ will be MEA. Testing will be carried out using MEA, followed by HTC's RS2 solvent. Polished flue gas from the FGD is passed through an amine solvent packed column where CO₂ is removed. The plant will have a capture rate of 90% and a capacity of around 100 tCO₂/d.

The pilot plant is the first of its size to be integrated into a live power plant in the UK and is intended to provide a bridge between small-scale pilots and commercial-scale demonstration projects. Plant operations began at the end of November 2011 and are expected to continue up to 2013. A total of £21 million is being invested in the project. It is anticipated that it will provide operating experience useful for the successful scale-up and deployment of the technology. Its application to a 385 MW CCGT plant in the UK is currently being investigated.

Planned RD&D activities

As with most other technology developers, HTC Pureenergy and its commercial partners are focused on minimising the energy penalty and costs associated with the capture process. To date, HTC has reduced associated capture costs and efforts are continuing with the aim of reducing them further (HTC, 2011). Major aims include:

- further development of designer performance (RS) solvents; to include new solvents such as mixed amines and engineered molecules;
- improvements to the liquid membrane absorber unit. Development of improved column packing and internals;
- development of new solvent reclaimer systems;
- improved process flow/design optimisation (TKO) through better heat integration, reduced steam requirement, and reduced process emissions;
- development of optimised FEED processes;
- optimisation of modular design and construction.

Alongside activities at the CCPilot100+ plant, a major focus of the RD&D programme will be on the HTC Pureenergy-Doosan Power Systems alliance at the ITC in Canada (HTC Pureenergy is ITC's

technology commercialisation partner). Here, the TKO amine-based capture plant process configuration will undergo a formal technology verification programme. Long term performance of HTC's RS solvents will form part of this. These will be assessed for degradation, heat stable salt formation, and propensity for corrosion within the various system components. Doosan is continuing with solvent development and testing on its Emissions Reduction Test Facility (ERTF) now modified to include solvent scrubbing. This is capable of capturing up to 1 tCO₂/d. Programmes will be undertaken to gain operational experience and obtain performance data, in particular, CO₂ capture rate and solvent regeneration energy for selected solvents over a wide range of process conditions. Testing will address the effects of process variables such as absorber inlet flue gas temperature, absorber inlet solvent temperature, lean solvent loading, solvent circulation rate, stripper bottom pressure, and reboiler steam pressure on system performance (Gardinera and others, 2011). Later testing may address the use of alternative structured and random packing materials and testing of alternative solvents.

HTC, in conjunction with some of its business partners (Doosan Babcock and Doosan Heavy Industries) is continuing efforts to validate and scale up its capture technology. Designs have been produced for a two-train capture facility, capable of producing 800 tCO₂/d. Doosan Babcock, jointly with its parent company Doosan Heavy Industries and Construction, has signed an exclusive global technology licensing agreement with HTC Pureenergy. Doosan Power Systems holds a global licence agreement with HTC, to offer their process technology in commercial-scale, post-combustion projects worldwide. Doosan Power Systems also owns a 15% share in the company (Gardinera and others, 2011).

In January 2012 it was announced that HTC Pureenergy had acquired Maxx Energy Solutions and created HTC CO₂ Systems Corporation. The intention is to supply on a commercial basis CO₂ capture and other gas processing systems.

3.2.5 Aker Clean Carbon

Aker Clean Carbon of Norway offers a commercial amine-based package known as the *Just Catch* process. Since 1980, Aker has supplied sixteen carbon capture units for hydrocarbon gases, as well as the treatment platform for the Sleipner natural gas project in the North Sea (1 Mt/y CO₂ capture). The technology is also being applied to industrial applications such as cement manufacture and refineries.

Projects

Aker Clean Carbon has been involved in a number of coal-based projects and proposals, although two of the latter have recently been cancelled. In the UK, together with Scottish Power, Shell and National Grid, the company was engaged in a project to develop a full-scale carbon capture facility at **Longannet power station**. As part of this, in May 2009, the consortium installed a 1 MW pilot plant at the site. This was subsequently operated successfully for >3000 hours. A main aim of the pilot programme was to provide the information needed to scale-up the technology. Between March 2010 and March 2011, a FEED study was carried out for a proposed larger project, with each consortium partner developing its own programme for this phase. These were then linked by an overarching programme, in order to manage the overall FEED timeline and key deliverables. The FEED scope was developed to meet the requirements of the UK CCS Demonstration Competition (Scottish Power, 2011). The proposed CCS facility was to capture (at least 90%) and store the CO₂ from the existing subcritical units at Longannet. The capture plant was to be connected to both Units 2 and 3, treating ~50% of the flue gases from either unit (but not simultaneously). Once captured, the CO₂ was to be transported using new pipelines and existing National Grid and Shell infrastructure from Longannet to the Goldeneye reservoir in the North Sea. However, late in 2011, the project was cancelled.

In Italy, Aker undertook a FEED study for ENEL's *Porto Tolle Carbon Dioxide Capture Unit Project*. The intention was for ENEL to build a post-combustion CCS demonstration project at the oil-fired

Porto Tolle power plant; this was to be converted to supercritical coal-firing but permission to proceed was revoked in May 2011. This project would have treated flue gases corresponding to 250 MW of electrical output, with the captured CO₂ (1–1.5 Mt/y) (TRL-8) stored in a deep saline aquifer under the north Adriatic Sea. Aker was to supply the carbon capture technology.

In late 2010, the company was awarded a contract to conduct a feasibility study for full-size retrofitting of EnBW's new coal-fired supercritical 912 MW power plant in **Karlsruhe**, Germany. Around 5 MtCO₂/y capture is suggested. The study is being produced in two phases. Phase I will include the development of a process design and estimates for the capital investment and operational cost of the CO₂ capture unit. Phase II will include integration and optimisation to the new coal-fired power plant, due on line in 2012.

Planned RD&D activities

The Aker Clean Carbon *Just Catch* development programme aims to:

- develop capture technology solutions in conjunction with end users;
- develop cost effective solutions for large-scale plants (coal-, gas- and biomass-fired power generation, refineries and cement plants);
- reduce process investment costs by 50%;
- reduce operating costs by 30%;
- reduce process-derived waste to a minimum;
- test new solutions at small- and medium-scale.

Alongside small-scale R&D, most of these issues are being addressed via a series of pilot plant-based projects, focused primarily on addressing technical issues and reducing cost.

A major area of development is concentrated on the selection of optimum amine-based solvents for the *Just Catch* technology. As part of this, Aker Clean Carbon is collaborating with SINTEF and the Norwegian University of Science and Technology (NTNU) in an eight-year development programme called SOLVit. In 2009, E.ON, ScottishPower and Statkraft also joined the programme. Major objectives include development of measures to reduce process energy requirements and environmental impacts, and the production of cost-effective solvents that are less corrosive and less prone to degradation.

In December 2011, Aker Clean Carbon signed agreements for the second stage of the SOLVit programme with support from Gassnova. E.ON and EnBW (Energie Baden-Württemberg AG) are industrial partners. This will include testing at EnBW's carbon capture pilot plant (300 kgCO₂/h) (TRL-6) located at the 816 MWe coal-fired **Heilbronn power plant** in Germany. During Stage 1 of the programme, two different reclaimer systems were tested and small-scale test rigs operated on different solvent systems using various flue gas compositions. More than 16,000 operating hours were achieved and seven major emission campaigns were carried out. About 45 different degradation products were identified by SINTEF, providing a better understanding of the chemistry in the capture process. During testing, advanced amine solvent systems were shown to be significantly less prone to degradation than a conventional 30% (wt) MEA solution. More than 80 solvent systems were screened and the best candidates selected for long-term pilot-scale testing during Stage 2.

Aker and the other SOLVit project partners are co-operating on the investigation into potential health implications when using large-scale amine-based capture systems; there have been concerns that emissions of species such as nitrosamines and nitramines could pose a hazard. As part of a comprehensive study (the Atmospheric Degradation of Amines (ADA) Project), researchers at the Norwegian Institute for Air Research and the University of Oslo have been studying the atmospheric chemistry of amine emissions to air (Bellona, 2011). Aker's pilot testing suggests that very low amine, nitrosamine and nitramine emission levels are achievable. Additional technology development and operation of demonstration facilities are likely to further reduce emission levels (*see* Section 6.5). During Stage 2, the programme will focus on the selection of the best solvent, undertake emission and

degradation measurements at pilot scale, and develop suitable emission control strategies. Efforts will also continue to address process scale-up issues and to reduce associated technical and commercial risks. As well as the proposed demonstration at Karlsruhe, in the USA, Aker Clean Carbon plans to continue its collaboration with the Southern Company to test and evaluate the Just Catch technology at the National Carbon Capture Center (NCCC) in Alabama.

To date, a 35% energy reduction in the carbon capture process appears achievable through a combination of improved solvents and process design. The technical target is to demonstrate a 50% reduction in energy demand by 2016, based on a reference case from 2008. Data generated from Aker's trials will be compared with that from other pilot-scale testing being carried out in Norway and the USA.

3.2.6 Cansolv® Technologies

Cansolv® Technologies Inc (CTI) was founded in 1997 as a Union Carbide spin-off to commercialise its regenerable SO₂ scrubbing system. The first Cansolv® SO₂ plants were commissioned in 2002. In 2008, Cansolv® was acquired by Shell Global Solutions International BV, a member of the Royal Dutch Shell group. There are currently fourteen units in operation with several more in the EPC phase. The Cansolv® CO₂ capture process has been demonstrated via >6000 hours of piloting operation (Shaw and others, 2012).

Cansolv® offers proprietary aqueous regenerable amine-based solvents for the selective or sequential removal of SO₂, NO_x, and CO₂. These are based on tertiary amines and promoters (probably piperazine and/or its derivatives) in order to yield sufficient absorption rates to be used for low pressure flue gas streams. The scrubbing by-product is water saturated with CO₂ that is recovered by steam stripping. Absorption rates comparable to MEA are claimed, but with 40% lower regeneration energy. Advantageously, the Cansolv® SO₂ capture system produces saleable H₂SO₄ by-product, instead of a solid waste requiring disposal. It also generates heat that can be used to provide part of the CO₂ solvent regeneration energy.

In operation, flue gas is first sent to the SO₂ absorber, then on to the CO₂ absorber before being fed to the stack with zero SO₂ and only 10% of the CO₂ remaining. The flue gas is first quenched and cooled in a pre-scrubber section, which is located in the SO₂ absorber. SO₂ and CO₂ are absorbed from the gas by contact with the Cansolv® solvents through sections of structured mass transfer packing in the absorption towers. Lean cool amine is fed to the top of each tower; in each, as the absorbents flow down the column (counter current to the feed gas), the pollutant is absorbed into the amine. The rich amine collects in the sump of the absorber tower and is pumped to the stripper for regeneration. As the absorption of CO₂ is an exothermic reaction, inter-stage cooling is employed (mid-tower) to remove this heat from the absorber tower, thus maintaining absorption efficiency. The rich absorbent is pumped to the regeneration tower through a lean/rich heat exchanger that recovers sensible heat from the lean amine. A reboiler uses low pressure steam to indirectly generate stripping steam which is injected into the bottom of the column. As the liquid solution flows down the tower, it meets the rising hot steam in sections of mass transfer packing where the heat reverses the absorption reaction and returns the SO₂ and CO₂ to the gas phase. In each case, the gaseous product is carried overhead and cooled in the respective stripper condensers where most of the steam condenses. Water-saturated product and product-saturated condensate are separated in the stripper overhead accumulator and the condensate is returned to the top of the stripper tower as reflux. The gaseous product leaves the stripper overhead accumulator and is delivered at positive pressure for downstream handling.

Projects

Cansolv®-based systems are currently in use in the oil and gas sector, and on sulphur plants, smelters, cokers and incinerators. They have also been piloted on several coal-fired plants in the USA and Canada (with ~12% CO₂ content in the flue gases). Several natural gas-fired boilers have been similarly treated.

At E.ON's 920 MW coal-fired **Heyden power plant** in Germany, a 7.5 MW pilot plant (TRL-6) is in operation. This fully modularised plant was pre-assembled and installed by Cansolv®. A major focus of the project is engineering development and testing. For the test phase (2–3 years), the plant will operate on a slipstream of ~20,000 m³/h of flue gas, representing nearly 1% of the power plant's total flue gas.

At SaskPower's **Boundary Dam power station** in Saskatchewan, Canada (Figure 10), the existing lignite-fired station is being revamped to incorporate a CO₂ capture pilot plant based on Cansolv® technology (the *Boundary Dam Integrated Carbon Capture and Sequestration Demonstration Project*). Approval was granted in July 2011 for the integrated carbon and sulphur capture system to be installed at the plant. This amine-based regenerable scrubbing system sequentially scrubs SO₂ and CO₂ in a single system, allowing capitalisation on internal synergies to recover energy and thus lower the overall energy demand. The Boundary Dam project aims to integrate and rebuild an existing lignite-fired unit to achieve a capacity of 150 MW (TRL-8). The current projection is that the plant upgrades will extend its useful power production life by 30 years. As part of this plant retrofit, an imminent requirement was to replace the steam turbine generator; by integrating the overall retrofit requirements with SO₂ and CO₂ capture implementation, significant savings are likely to be achieved, compared to addressing separately the need for sulphur and carbon capture. When completed, the integrated carbon capture plant will capture >1 MtCO₂/y, reflecting a 90% capture rate for the 150 MW coal-fired unit. Additional benefits will include the integration of an SO₂ capture process that will provide feedstock for a 50 t/d sulphuric acid plant, providing a key feedstock for the local fertiliser industry. Features specific to the Boundary Dam project include:

- efficient cooling equipment upstream of the Cansolv® plant that will provide a very cool gas, hence improve overall performance of the system;
- a locally available cool water source that will help provide optimal temperatures for the capture plant;
- the SO₂ and CO₂ scrubbing will be housed in the same structure; as they are sequential, they have been essentially designed as one block;
- heat integration – the Cansolv® system will recover energy from the SO₂ scrubbing section and use it in for the CO₂ capture section (using Mechanical Vapour Recompressors);
- as both absorbers operate at atmospheric conditions, significant costs savings will be realised by opting for less expensive materials of construction (such as concrete lined with acid resistant tiling to withstand the wet scrubbing environments);
- the towers have been designed as rectangular vessels rather than cylinders. This simplifies design and supply of the mass transfer packing.

SNC-Lavalin is providing EPC services to the project. Construction is under way and is scheduled to be completed by May 2013. The installation of the new steam turbine is scheduled to be completed by September 2013, with hand-over to the client by December of the same year. Capture operations are planned to begin in 2014 (Carbon Capture Journal, 2011). Cansolv® is supplying the carbon/sulphur



Figure 10 The Boundary Dam power plant in Saskatchewan, Canada (photograph courtesy of SaskPower)

capture process design technology; this will use Cansolv® DS solvent to achieve 100% SO₂ capture upstream of the Cansolv® DC103 CO₂ capture system.

In December 2011, it was announced that the government of Saskatchewan had approved construction of the project and that SNC-Lavalin had started engineering and procurement activities. By early 2012, major components such as the CO₂ stripper, were being installed on site. The

total cost of the project was cited as US\$1.24 billion. A decision has yet to be made on whether to retrofit Units 4, 5 and 6 at Boundary Dam for CCS. The future of these units will be decided once Unit 3 has been completed and SaskPower has been able to evaluate the effectiveness of the capture technology. Units 1 and 2 will shut down in the next few years, as they are viewed as too small to justify a retrofit.

In the UK, Cansolv® Technologies and RWE npower have built a 3 MWe integrated SO₂ and CO₂ capture pilot plant at the **Aberthaw power station** in South Wales, where around 50 t/d of CO₂ will be captured from a slipstream. Both parties are contributing to the overall project costs. Cansolv® designed and supplied the technology, the absorbents and the modularised integrated SO₂/CO₂ capture plant.

The main project objectives (Shaw and others, 2011) include:

- provision of a controlled environment to allow performance optimisation of CTI's integrated capture technology;
- demonstration of the technology's claimed lower operating costs;
- demonstration of the improved performance of new generation CTI absorbents;
- demonstration of the operational flexibility of the capture plant, including cold and hot start up times;
- validation of in-house modelling and optimisation tools.

Fabrication was completed in June 2011 and the installation completed in December of the same year. Major plant components were fabricated in China. Commissioning and start-up was achieved in April 2012. The plant is scheduled to operate for a two-year test period. The ongoing development programme will assess the system's operational flexibility and will include a programme of start-stop and ramping cycles. Process optimisation studies will be carried out to address energy requirements, CO₂ purity and capture rates. In addition, the performance of main plant components will be monitored as well as the impact of degradation on waste substances, solvent stability and consumption (RWE, 2011). Plant reliability and operability will be assessed and improved maintenance and control procedures developed. The precise solvent formulation being used will remain commercially confidential. The testing of a new solvent formulation will begin in April 2013.

Planned RD&D activities

Cansolv® Technologies is active in a number of areas and it is anticipated that many outstanding development and technology scale-up issues will be addressed by the successful operation of the Boundary Dam and Aberthaw pilot units. There is a major R&D focus on developing improved, more effective solvent formulations for capturing CO₂ and other species from different flue gases. Cansolv® is continuing its developing programme for high performance solvents for NO_x, mercury and CO₂ capture. As part of this programme, a new solvent (absorbent DC201) is being developed and evaluated. Testing suggests that this will exhibit improved performance over the existing DC103 solvent; it has better loading capacity, lower heat of reaction, lower amine regeneration energy and lower cooling requirements. These attributes should help reduce both capital and operating costs. DC201 has increased CO₂ loading capacity, which will allow a reduction in liquid circulation rate, and a lower contribution of the sensible heat and latent heat components in the regenerator. CTI expects amine regeneration energy savings of ~ 20% (compared to DC 103) (Shaw, 2012; Shaw and others, 2011).

Efforts are being focused on the increased commercialisation of Cansolv® technology by improving process economics. As with other technologies, attempts are being made to reduce process costs; a major goal is to reduce regeneration heat requirements. Cansolv® is examining ways that this might be achieved by combining CO₂ capture in a single column with processes for capturing pollutants such as SO₂ and mercury. Ways to improve plant heat integration and other optimisation measures are also being pursued.

3.2.7 Hitachi

Since the early 1990s, Hitachi has been developing an amine-based capture system for coal-based applications. Extensive development led initially to the introduction of the H3 proprietary solvent. A two-year pilot scale test period was undertaken at TEPCO's **Yokosuka Thermal Power Plant** in Japan where a slipstream was treated. H3 and other amines were tested (>2000 hours) and their performance compared. H3 has now had several thousand hours of operational testing and more than 90% CO₂ capture has been achieved. H3 is claimed to have specific regeneration energy (2.8 MJ/kg CO₂) much lower than most commercial MEA solvents. It also has high absorption capacity, requiring a lower liquid:gas ratio for 90% capture compared to MEA (Eswaran and others, 2011). Thus, operating costs should be lower.

Projects

The company is currently co-operating with Electrabel/GDF Suez and E.ON to develop and operate a 5 MWth CO₂ (TRL-6) capture test facility (the Large Mobile Pilot Plant) primarily for solvent testing. The main aims are to undertake scrubbing tests under real flue gas conditions with different chemical solvents, and the generation of data necessary for the further development of design concepts for both new-build and retrofit power plant situations.

As the main plant components are transportable, the mobile test facility will be alternated between different sites at Electrabel's and E.ON's power plants in Germany, The Netherlands and Belgium. In operation, the unit is installed at the host power station downstream of the FGD unit. A four-year programme of testing is now under way. It is anticipated that the data generated will contribute towards process scale-up and help support the design of demonstration and commercial plants. A major aim is system optimisation in order to reduce efficiency losses. The approach being taken comprises three essential elements:

- the use of the latest solvent formulation with low regeneration energy and resistance to degradation (and also the continued development of next generation solvents with improved performance);
- rational redesign and modifications of the steam turbine to supply the heat for CCS with minimum loss of electricity output;
- integration involving boiler heat recovery, combustion air preheating, feedwater heating, and turbine condensate preheating in the context of CCS implementation.

Through application of these measures, it is anticipated that plant efficiency losses can be reduced significantly (Song and others, 2010).

In March 2012, SaskPower of Canada announced that it was to partner with Hitachi Ltd to construct a US\$60 million carbon capture test facility (CCTF) at its **Shand Power Station** in southeastern Saskatchewan. The CCTF will allow international developers to fully evaluate performance of their systems in capturing CO₂ from coal-fired thermal power plants. The unit is being built to accommodate a wide range of test configurations, ensuring it should remain a viable facility for many years. SaskPower and Hitachi are each contributing ~US\$30 million to the project, with SaskPower acting as owner/operator. Construction will begin in late 2012 or early 2013, with a scheduled completion date of summer 2014. Hitachi will supply their experienced process development team, core process equipment, and their proprietary amine capture solvent. SaskPower expects to evaluate a number of current and emerging carbon capture technologies over the lifetime of the facility.

Planned RD&D activities

Alongside pilot testing at the Shand station in Canada, Hitachi will continue refining new solvent blends. New formulations will be tested and compared with other commercial or near-commercial solvents by independent institutions in Europe, Japan and USA. Part of its programme in the latter (announced in August 2011) includes co-operation with the University of Kentucky Research Foundation. This will involve the development and testing of an innovative heat integration method

that uses waste heat from the Hitachi H3-1 advanced solvent carbon capture system, while improving steam turbine efficiency. The programme will also implement a process concept (working with the heat integration method) to increase solvent capacity and capture rate in the CO₂ scrubber. H3-1 is the latest refinement of the H3 solvent formulation. It is claimed to have the same advantages of high CO₂ absorption capacity and low regeneration heat as H3, but with lower amine loss. Pilot-scale testing of H3-1 carried out by the University of North Dakota confirmed that a 90% CO₂ capture rate was achievable under a range of operating conditions. For this level of capture, the solvent recirculation rate required (compared to 30% MEA) was ~45% lower and the energy required to regenerate the H3-1 was ~30% lower. Further pilot-scale testing is also planned at Babcock-Hitachi's Kure Research Laboratory in Japan.

3.2.8 Toshiba Corporation

Since 2006, Toshiba of Japan has been active in the development and testing of an amine-based carbon capture system, claimed to be more energy efficient than many alternatives. The company has established a CCS development and promotion organisation and is actively seeking to further accelerate the commercialisation and deployment of its technology. With this aim in mind, recently, research and development efforts were increased to support early establishment of this area of business. The goal is to establish a business capable of meeting emerging needs for commercial-scale CCS systems for thermal power plants by 2015.

Projects

As part of its ongoing development programme, the company built a 10 t/d CO₂ capture pilot plant. (TRL-6) This was completed in 2009 and treats a flue gas stream from the coal-fired **Mikawa power plant** in Fukuoka. Flue gas is introduced into the pilot downstream of the power plant's FGD. This is treated to further reduce SO₂ levels then fed to the pilot plant's absorber.

By the end of 2011, the pilot had operated for more than 4300 hours; operation had been stable and CO₂ capture rates higher than expected. Flue gas with a CO₂ concentration of ~12% was treated at a flow rate of 2100 m³/h. A range of solvent compositions had been assessed and a number of candidate solvents selected and evaluated; these included newly developed amine solvents (TS -Toshiba Solvents). Pilot plant testing determined that several solvent mixtures had lower energy requirements (~2.5–2.6 GJ/t of CO₂) than conventional MEA solutions. For instance, the value for TS-1 was claimed to be ~37% less than that of conventional MEA. Reportedly, this is the first time in the world that energy consumption significantly below 2.8–3.0 GJ/t of CO₂ has been attained at a 10 t/d pilot-scale plant using real coal-derived flue gas. The pilot plant has since been the subject of several redesigns in order to reduce energy requirements further. It is now considered that for a larger-scale commercial plant, energy requirement could now be reduced to 2.3 GJ/t of CO₂ (Ohashi and others, 2011). During 3000 hours of testing, it was found that the concentration of degradation products, such as carbonic acid, was lower than encountered when using MEA.

Planned RD&D activities

Future RD & D will focus on a number of areas (Ohashi, 2011):

- continued screening of potential new solvents that will include amino-based derivatives. The aim is to reduce energy consumption and enhance solvent durability and reliability;
- addressing concerns about the possible environmental effects of amine solvents. The level of emissions will be examined and means for their control developed. As part of this, emission levels will be monitored during pilot plant testing;
- verification of improved process and environmental performance aspects regarding future commercial-scale capture plants integrated with power generation;
- continuation of design for a full scale demonstration plant using data from pilot plant verification testing. Heat loss tests and analysis suggest that a value of 2.3 GJ/t of CO₂ would be possible on larger-scale commercial plants.

Toshiba will continue to concentrate its development efforts on post-combustion capture as it considers this technology to have the best potential for both new-build power plants as well as retrofit situations (Ohashi and others, 2011). The company aims to supply low cost CCS systems for application to thermal power plants. It is anticipated that this will be achieved by increased integration of power generation, and enhanced flue gas treatment and CCS systems.

3.2.9 Babcock & Wilcox 'OptiCap' process

OptiCap technology has been developed over a six-year period using the company's own Regenerable Solvent Absorption Technology (RSAT) test facility. Rather than producing novel materials, B&W has concentrated its research efforts on developing an effective blend of existing solvents (probably amine-based) and other chemicals. OptiCap is claimed to be capable of capturing ~90% of CO₂ from flue gases.

The RSAT test facility can capture up to ~7.5 tCO₂/d (TRL-6) from flue gas. Pilot testing of the OptiCap solvent has shown favourable performance characteristics. Compared to 30% MEA, OptiCap has demonstrated lower reboiler heat duty, better resistance to degradation, higher mass transfer rate, and higher CO₂ carrying capacity. These factors should help provide additional savings in capital and operating costs (a major focus) but need to be confirmed in future larger scale test campaigns. B&W considers that there are further savings still to be made and has simulated several process design cases that could further reduce the associated energy penalty through improved heat integration with the power plant. Reportedly, some of these design cases are specifically related to the unique properties of the OptiCap solvent, such as its ability to regenerate at higher temperatures and pressures. These designs will be developed further through a programme of pilot-scale and field testing.

Projects

A test programme at the US National Carbon Capture Center is planned for the evaluation of OptiCap.

Planned RD&D activities

Although to date, B&W has paid the technology development expenses, the testing at the National Carbon Capture Center will be funded in part by the federal government. OptiCap will be evaluated during a three-month test campaign. This work is expected to add to the existing body of knowledge by providing long-term operating experience when using coal-derived flue gas. Areas to be addressed during the test campaign will include (Poling and others, 2011a):

- extent of resistance to oxidative degradation;
- extent of resistance to thermal degradation – testing so far has shown OptiCap to be stable at operating temperatures up to 150°C. This offers the potential for regeneration at higher operating temperatures and pressures, which could lead to significant energy savings in terms of CO₂ compression;
- ease of reclaiming – thermal reclaiming is likely to be the primary technology for removing degradation species formed;
- examination of solvent volatility. OptiCap has lower volatility (compared to 30 wt% MEA), thus reducing solvent losses and decreasing energy requirements;
- increased mass transfer rate – the rate of absorption of CO₂ for OptiCap is approximately twice that of 30 wt% MEA;
- examination of increased CO₂ carrying capacity. As OptiCap can be loaded with approximately twice the amount of CO₂ per unit of solvent, the solvent recirculation rate is decreased.

Following the test campaign at the National Carbon Capture Center, B&W and others will review how well OptiCap has performed. If the outcome is positive, the company will seek a larger, commercial-sized demonstration. In readiness, a suitable host site is being sought; the plant size is flexible although the company's 75 MW reference plant design is considered to provide an effective combination of scale and cost. Whilst supplying the necessary technical design data for scale-up to

larger units, the modest size will provide the required information at a reasonable cost (Poling and others, 2011b). While the search for a demonstration host site proceeds, the research team is continuing its work to develop new solvents and enhance existing designs. The team will continue to develop and optimise the plant design and layout in an effort to reduce both capital and operating costs.

In December 2011, it was announced that B&W had been awarded US\$2.8 million by the US DOE to study chemical formulations to improve the performance of its RSAT process solvent. B&W will contribute US\$0.7 million in the form of in-kind research and development to the work that will be undertaken at its research centre in Barberton, Ohio. This DOE-funded project will allow the exploration of new options for improving the energy requirements for solvent regeneration, durability and other factors to make the OptiCap solvent an attractive option for post-combustion CO₂ capture. Project participants also include the University of Cincinnati and FirstEnergy Corp.

3.2.10 Other major technology developers and projects

There are a number of other organisations active in the development and supply of advanced amines and amine-based processes. In some cases, projects are being taken forward by commercial consortia. For instance, since 2009, RWE, Linde Group, and BASF have been co-operating on carbon capture through the operation of a pilot plant at RWE's lignite-fired Niederaussem power station in Germany (see Figure 11). Linde was responsible for pilot plant engineering and construction. BASF is using the pilot plant to test a newly developed capture process based on improved proprietary solvents.



Figure 11 The Niederaussem power station in Germany (photograph courtesy of RWE)

Commissioned in July 2009, the plant treats 1550 m³/h of flue gas and captures up to 7.2 tCO₂/d. (TRL-6). Capture rate is 90%. A programme of testing of several solvent formulations began in 2009. The first phase of testing has been completed successfully – over an 18 month period, some 10,000 hours of operation was carried out. Plant availability was in excess of 97%. The plant was operated using MEA during 2009, and new scrubbing solvents (Gustav 200 and Ludwig 540) during 2010-11. Both

of these showed a 20% lower specific energy consumption (compared to MEA) as well as lower solvent circulation rates. They also exhibited improved oxygen stability and lower solvent consumption.

As part of Phase II of the project, the partners are carrying out longer-term tests at Niederaussem. This new phase will run from March 2011 until the end of 2013. One of the new solvents has been selected for this demonstration. During this phase, the pilot plant will be modified by the installation of high-performance column internals in the absorber, an improved emission control system at the top of the absorber, and additional online gas analysis equipment. In two long-term tests (each of around a year), the first with flue gas feeding from a conventional FGD plant, the second with flue gas feeding from a high performance FGD unit, long-term behaviour will be tested with emphasis on degradation, reclaiming and emission behaviour (Moser and others, 2011; Schmidt, 2011). Materials testing is also being undertaken, examining a range of different components and materials of construction. This includes different steels and polymers. So far, all of the steel types tested have been found to be capable of resisting localised corrosion. The project partners have concluded that the results of the testing programme have shown that the goal of an efficiency loss of less than 10 percentage points for a

power plant with CCS is achievable using the capture technology being tested at Niederaussem. The pilot plant results should reduce design uncertainties for implementation of full-scale capture projects. It is therefore considered that a demonstration plant could be implemented on the basis of the available results.

Elsewhere in Europe, launched in March 2012, IFPEN (IFP Energies Nouvelles) of France is co-ordinating a multi-partner project (the Octavius Project) aimed at significantly increasing the energy efficiency of current capture technologies in order to reduce process costs. The project brings together sixteen other partners: TNO, Sintef, NTNU, Ineris, DTU, TUHH, E.ON, EnBW, Doosan Power Systems, ENEL, Laborelec (GDFSuez), EDF, Prosernat, TIPS, EcoMetrix and Eskom. The five-year project's main objectives are:

- To prepare for the first CCS demonstrations at utility scale, implementing first generation capture processes based on amine-type solvents. Three capture pilot units (the CATO unit in Maasvlakte, the ENEL unit in Brindisi, and the EnBW unit in Heilbronn) will be used to test the operability and flexibility of first generation processes.
- To demonstrate the DMX second generation post-combustion capture process (on an industrial scale) developed by IFPEN. The DMX process uses a solvent claimed to be capable of reducing the energy for solvent regeneration by almost 40%. This will be tested on the ENEL pilot unit.

Initial first technical and economic assessments suggest that, when applied a coal-fired power plant, the DMX capture technology reduces the energy penalty by 2 percentage points, thereby cutting the costs associated with CO₂ capture by 20%. The project budget is €13.5 million, €8 million of which will be provided by the European Commission.

In the USA, as part of a NETL-managed programme aimed at developing CCS systems capable of achieving at least 90% CO₂ capture rates, with a cost of electricity increase of no more than 35%, Linde will carry out a development programme using a 1 MWe slipstream pilot plant at the National Carbon Capture Center. This will evaluate a novel amine-based process developed by BASF.

Globally, there are also several major projects being developed that are likely to feature post-combustion capture although details have not yet been made public. For instance, in Western Australia, Aviva Corporation and partners are developing a proposal for a commercial scale power plant (at Coolimba) based on two 200 MWe (or possible 3 x 150 MWe) generating units using CFB boilers. From the outset, the project will be constructed as carbon capture-ready to facilitate the integration of a ~100 MW CCS project. The plant will operate on base load, supplying electricity to major customers in the mid-west region and the grid. A commissioning date of 2014 and start-up date of 2015 have been suggested. Reportedly, adoption of an amine-based system seems likely. The project is being designed with the potential to capture and store up to 90% of its CO₂ emissions, and incorporates plans to phase in up to 2.9 Mt/y CO₂ capture for up to 30 years. This will be taken forward as a separate project, when deemed feasible. A number of possible CO₂ storage sites are being evaluated that include depleted gas reservoirs at Woodada and Dongara. A CO₂CRC study suggests that these have a CO₂ storage capacity of 30 to 40 Mt (Harris, 2009). There is also potential for EOR use in the Dongara oilfield. Other possible sites include formations in the North Perth Basin where potentially, up to 500 Mt could be stored in deep saline formations. Australia's Environmental Protection Authority and Environment Ministry have both approved the project.

3.3 Commercial coal-fired plants featuring post-combustion capture

There are a handful of coal-fired power plants that deploy post-combustion capture as part of their commercial day-to-day operations. Two are located in the USA and are operated by AES. These are the 320 MW Shady Point Power Station in Oklahoma, and the 180 MW Warrior Run Power Station in Maryland. Both use coal-fired CFB boilers and both absorption plants use MEA-based capture

systems supplied by ABB Lummus. At Shady Point, prior to CO₂ capture, the SO₂ concentration in the flue gas is reduced from 500 ppm to 2 ppm by scrubbing with sodium hydroxide. The facility produces 200 tCO₂/d of used for food processing, freezing, beverage production and chilling purposes. The plant started up in 1991 and reportedly, has operated with few problems. This has been limited to minor corrosion, even though the capture unit was manufactured largely from mild steel. The original absorber packings are thought to still be in use. As built, the capture unit was equipped with an anti-foaming plant although this has never been used. The CO₂ capture plant at Warrior Run was commissioned in 2000. Here, CO₂ is captured and used for several applications that include food processing and related processes, fire extinguishers, and dry ice production.

The USA also hosts the longest-running CO₂ capture plant operating on a coal-fired unit. This is the Searles Valley Minerals Plant in Trona, California, which uses an ABB Lummus MEA unit to capture CO₂ from an on-site coal-fired cogeneration plant. As part of the commercial process for producing sodium carbonate, the captured CO₂ is used for the carbonation of brine. Approximately 800 t/d of CO₂ is captured from the cogeneration plant's flue gas. The Trona plant started operation in 1978.

In China, CO₂ is being captured from several coal-fired power plants and sold for various commercial applications. Since 2008, an amine-based pilot plant has been in operation at the 800 MW Gaobeidian cogeneration plant. Here, CO₂ is captured (~3 kt/y) (TRL-6) and sold for food and beverage applications. Partners involved in the programme comprise China Huaneng, CSIRO (of Australia), and the Thermal Power Research Institute (TPRI). The plant was designed by North China Power Engineering Co Ltd and supplied by TPRI. It is located on a sidestream after the deNO_x SCR, ESP and FGD units, and treats 1% (2000–3000 m³/h) of the plant's flue gas. Steam consumption is 3 GJ/t CO₂ and solvent consumption <1.35 kgCO₂/t. The capture solvent is a mixture of ethanolamine and additives. Quality of the CO₂ produced is 99.9%; this is used mainly for carbonated beverage production.

Data generated by the Gaobeidian plant operations were used to scale up the technology for a larger project located at the 1320 MW Shidongkou No. 2 Power Plant in Shanghai. Construction began in 2009 and the capture plant entered service in 2011. This scrubs CO₂ from flue gases for a cost per tonne far below prices elsewhere. The capture system removes ~120 kt/y of CO₂ (TRL-8) from 3–4% of the facility's flue gases. Food grade CO₂ (>99.9%) is produced and sold. The plant has two storage tanks that can hold ~1200 tCO₂, the amount produced every 100 hours of operation. When demand falls below the tanks' capacity, the capture plant is switched off. Huaneng claims that the cost for capturing the CO₂ is less than 30 US\$/t, rising to 35 US\$/t when the gas has to be purified for use in the food and beverage industry (Minchener, 2011). This is some 30% of the cost quoted for OECD intended projects. Although Huaneng has not yet revealed all the technical details of its CCS process, it has reported that the company has made unspecified changes in the design of the plant and the chemistry of the solvent that have increased the energy efficiency of the system by 11–14% and reduced the cost of installation (Nature, 2011). The project's lifetime is not fixed; CO₂ capture costs are covered by its sale, hence the sidestream project could continue for some time. Huaneng also intends to offer access to the plant to potential overseas partners with alternative CO₂ capture solvents that require testing under realistic coal-fired power plant conditions (Minchener, 2011).

In a further development, in February 2012, it was announced that China Huaneng Group and Duke Energy of the USA had signed a new, three-year agreement expanding their research co-operation in the areas of advanced coal and CCS technologies. The two parties initially signed a MoU in 2009 to pursue high-level discussions and information sharing on a number of clean-energy fronts. Based on experience gained from the Shidongkou station, the expanded agreement proposes an engineering study to determine the potential feasibility of applying Huaneng's carbon capture process at Unit 3 of Duke Energy's 3.15 GW Gibson Station in Indiana. Funding is being provided by the US-China Clean Energy Research Center (CERC).

Since 2010, a sidestream CO₂ capture test facility has been operating at the (2 x 300 MW subcritical)

coal-fired Hechuan Shuanghuai Power Plant in Chongqing, owned by the China Power Investment Corporation (CPIC). Slightly less than 1% of the plant's flue gas is being treated, producing around 10 kt/y of CO₂. Currently, the capture solvent used is MEA. Captured CO₂ is sold on, mainly for welding applications. It is planned to upgrade the capture system to a capacity of 100 kt/y (TRL-8). At the same time, R&D is being undertaken to improve the absorbent effectiveness of the MEA. The possibility of increasing the purity of the captured CO₂ to achieve the food grade standard (>99.99%) is also being assessed (Minchener, 2011).

An amine-based project belonging to Sinopec has also been operating since mid-2010. This captures 30 ktCO₂/y (TRL-7) from the flue gases of the coal-fired Shengli Power Plant. The CO₂ stream is >99.5% pure and is sold on for EOR purposes in the Shengli oilfield, China's second largest (Sizhen, 2011). Around 80 tCO₂/d is being injected.

The China Guodian Corporation is setting up a 20 kt/y CO₂ capture and utilisation industrial pilot plant at the Tianjin Beitang power plant. The captured CO₂ will be further treated to provide a food grade product for sale in Tianjin. The unit is expected to be operational by the end of 2012.

Since 1994, the Sumitomo Chemicals Plant in Japan has been using a Fluor Econamine FG CO₂ scrubber system to treat flue gases generated from on-site gas and coal/oil-fired boilers. It produces around 150–165 t/d of food-grade CO₂. Engineering and construction was carried out by Mitsubishi Heavy Industries on a turn-key basis (under Fluor licence and supervision). The maximum flue gas volume treated is ~36,500 m³/h.

A summary of major coal-fired amine-based post-combustion capture projects is presented in Table 12.

3.4 Future RD&D focus and challenges – amine-based systems

For the near- to mid-term, much industry effort will continue to be focused on the absorption of CO₂ into solvents. This reflects the fact that much of today's industrial CO₂ capture chemistry knowledge and process experience has been based heavily on absorption processes.

The largest area of post-combustion development is currently centred on the use of amines and amine-based derivatives and processes. Even though some amine processes have been used for many years, there is still potential for process enhancement and improvement and these goals are being pursued by a number of technology developers. Various routes aimed at improving process efficiency and reducing costs are being followed. Alongside modifications to the chemical properties of the sorbents, research is also addressing the physical structure and scale-up of absorber and regenerator equipment, examining membrane contactors to improve gas-liquid contact and/or heat transfer, and optimising thermal integration with steam turbine and balance-of-plant systems. The environmental impacts of solvents and solvent degradation products are also coming increasingly under scrutiny. Recently, efforts to address these issues have increased, with work being undertaken by Gassnova and the GCCSI/CSIRO; the latter focused on assisting the permitting of solvents protected by intellectual properties.

At the moment, most major development goals revolve around reducing the relatively large parasitic load that CCS imposes on a power plant; the majority of this is for CO₂ capture, particularly the energy needed to regenerate the solvent (Stoeber, 2012). In an effort to overcome this, numerous RD&D projects are under way aimed at developing improved chemistry, developing new process designs, and devising novel power plant integration schemes – most are focused on minimising process energy requirements. In general, this takes precedence over other issues such as reducing CAPEX, solvent degradation and volatility. These are sometimes viewed as being secondary to the prime issue of reducing parasitic load. Typically, there is a penalty of ~10 percentage points in

Table 12 Major coal-fired, amine-based post-combustion CO ₂ capture projects							
Country	Project	Lead organisation(s)	Plant/capture facility, MW	CO ₂ fate	Proposed start-up	Comment/status	Estimated TRL
Australia	Tarong pilot	Tarong Energy, CSIRO		1500 t/y No storage	Pilot started up in 2010	Operations until 2011	6
	Loy Yang	Loy Yang Power, CSIRO, Int Power	2100	1000 t/y	Pilot started up in 2008	Brown coal fired Solvent testing	6
	Coolimba	Coolimba Power (CFBC technology)	300–400	Up to 2.9 Mt/y Depleted oil/gas	2015	–100 MW CCS project proposed Possibly amine-based	8
Canada	Bow City	BCPL	1000	1 Mt/y EOR	2016	Subbituminous coal fired	9
	Genesee	Capital Power	150	1 Mt/y. Saline aquifer or EOR	2015	Subbituminous coal fired	8
	Boundary Dam	SaskPower	150	1 Mt/y EOR	2014	Lignite-fired Cansolv® amine technology	8
China	Huaneng Beijing Gaobeidian Cogen	Huaneng Group, CSIRO, TPRI	845	3 kt/y	Pilot started up in 2008	Sidestream CO ₂ sold for commercial uses	6
	Hechuan Shuangui Power Plant	CPIC	600	10 kt/y	Start-up 2010	MEA solvent used. CO ₂ sold for commercial uses	7
	Shi-Dong-Kou Second power plant, Shanghai	Huaneng Power	1320	120 kt/y	2011	Scale up of Gaobeidian technology. CO ₂ sold for food and beverage use	7–8
	Shengli Power Plant pilot, Dongying	Sinopec		40 kt/y EOR	2010	May later be increased to 1 MtCO ₂ /y capture	7
Czech Rep	NW Bohemia clean coal project	Multi-partner	250	1.6 Mt/y	2015	Lignite fired Possibly amine-based	8–9
Denmark	Esbjerg, CASTOR pilot		420	1000 kg/h	Started up in 2006	Slipstream Developments ongoing under other EU projects	6
	Norjyllandsvaerket Unit 3	Vattenfall	600		2013	Pilot	6

Table 12 – Continued							
Country	Project	Lead organisation(s)	Plant/capture facility, MW	CO ₂ fate	Proposed start-up	Comment/status	Estimated TRL
France	Le Havre	EdF, Alstom, Dow	600	25 t/d No storage	2012	Advanced Alstom/Dow amine process	6
Germany	Niederaussem	RWE, BASF, Linde	1000	7.2 t/d	Two phase programme. Pilot started up in 2009	Solvent and equipment testing	6
	Heyden	E.ON, Cansolv®	920		2011	7.5 MW pilot Cansolv® technology Process optimisation studies – 2–3 years	6
	Wilhelmshaven	E.ON, Fluor		3 t/h	2010	5 MW pilot. Econamine FG+. >90% capture rate	7
	Jaenschwalde	Vattenfall	3000	2.7 Mt/y Saline	2015	Lignite fired. Also considering oxyfuel. But put on hold (Sept 2011)	9
Italy	Federico II plant, Brindisi – CCS1 pilot	ENEL, ENI	48	5 kt/y Depleted gas/saline		Pilot work started in 2009. Plant started up in 2010. MEA and other solvent testing	6
	Porto Tolle	ENEL	250	1–1.5 Mt/y Saline	2015	Equivalent of 250 MW to be treated. But permission for converting oil-fired power plant to coal revoked in May 2011. 'On hold'	8
Japan	Nagasaki	MHI	1500	10 t/d	Pilot started up in 2006	MHI solvent development	6
	Mikawa power plant, Fukuoka	Toshiba	47.5	10 t/d	2009	Solvent and process testing	6
S Korea	Korea-CCS1	KEPCO	300–4000 CFBC or 500 MW PCC plant	1.5 Mt/y Saline	2017	Feasibility completed by 2014	9
Netherlands	Maasvlakte, Rotterdam	E.ON, GDF Suez, Electrabel	~250	1.1 Mt/y Depleted gas field	2015	250 MW scale project. Fluor Econamine. Part of the Rotterdam Climate Initiative	8
	Eemshaven	RWE	1600	Depleted oil/gas	2015	Pilot. Possibly amine-based	7

Table 12 – Continued							
Country	Project	Lead organisation(s)	Plant/capture facility, MW	CO ₂ fate	Proposed start-up	Comment/status	Estimated TRL
Norway	Husnes	Sargas	400	EOR	2015		7
Poland	Belchatów	PGE, Alstom, Dow, PIG, Schlumberger	Phase II – 260	Phase I – 0.1 Mt/y Phase II – 1.8 Mt/y Saline or EOR	2015	Alstom/Dow amine. Larger unit on new SC plant by 2015. But present project status unclear	7
Portugal	Pego power plant	Tejo Energia, EdF, EDP, ENDESA	600			Possibly amine-based	–
UK	Longannet	Scottish Power	2400	2 Mt/y EOR	2014	Aker Clean Carbon pilot started up in 2008. Larger project from 2014. But project cancelled in 2011	6
	Aberthaw	RWE, Cansolv®	1500	50 t/d	2011	3 MW pilot project. 2010. 2 year test period	7
	Tilbury	RWE	1400			Scale up of Aberthaw proposed. Cansolv®	8
	Ferrybridge, 5 MW CC Pilot 100+ project	SSE, Doosan Babcock, Vattenfall, UK Coal	500	100 t/d Depleted oil	2011	HTC Purenergy process. Solvent testing. Operation 2011-12	6
USA	Plant Barry, Mobile, Alabama	Southern Company	2660	500 t/d EOR or saline aquifer	2011	25 MWe pilot. MHI KM-CDR Kansai system. Larger scale second phase project on hold in March 2010	7
	WA Parish	Powerspan/ NRG Energy	60 MW slipstream. May increase to 240 MW	60 MW – 400 kt/y 240 MW – 1.6 Mt/y EOR	Commission 2014	Fluor Econamine FG+	7
	Nelson 6 CCS project, Louisiana	Tenaska/ Entergy	na	3.6 Mt/y	2015 but on hold	n/a	8
	Trailblazer, Texas	Tenaska	800	5.75 Mt/y EOR	2015-16	Fluor Econamine FG+	9
	South Charleston pilot, West Virginia	Alstom, Dow Chemical	1800 t/y. No storage	Pilot to start up late 2011	Dow Carsol FGL advanced amine	Two year test programme	7

efficiency loss with current (MEA) capture technology. A longer term industry R&D target (beyond 2030) is to reduce this to below 5 percentage points (ZEP, 2010a).

A number of major R&D programmes are focused on developing advanced amine-based solvents and

processes capable of reducing process costs, improving energy efficiency, enhancing liquid-gas contacting, and developing more effective solvent formulations. For instance, in the USA, various DOE projects aim to develop post-combustion capture (and oxyfuel) technologies capable of achieving at least 90% capture, whilst limiting increases in the cost of electricity to no more than 35%. For pre-combustion systems, the aim is for a maximum of 10%.

There are a number of development programmes under way aimed at enhancing amine properties such that their capture performance is improved and the associated operating costs reduced. For instance, in the USA, Akermin is developing an advanced low-energy enzyme catalysed potassium carbonate-based solvent (carbonic anhydrase) for CO₂ capture. This reaction rate should be higher and the regeneration energy required, considerably lower, than that of conventional amines. The principal project objective is to demonstrate 90% CO₂ capture from simulated flue gas at rates comparable to MEA. Testing is under way using a closed-loop bio-reactor capable of processing up to 500 L/min of simulated flue gas, roughly the equivalent of a 5 kWe power plant. Operation will be assessed over a six month period of continuous operation. A detailed Aspen model is being developed and extrapolated to a power plant equivalent of 550 MWe; this will include mass and energy balances, electric power requirements, and projected chemical and maintenance costs.

In Australia, CSIRO is also developing potassium carbonate capture system (the CO₂CRC Uno Mk 3 Project). CO₂CRC is using a dedicated capture plant at the International Power GDF Suez Hazelwood power station to develop its innovative capture system. Funding from the Victorian Government and BCIA is supporting the project.

A number of areas have been identified as having the potential to improve efficiency and/or reduce costs (VGB, 2004; ZEP, 2010a; GCSSI, 2012d; GCSSI, 2012e). Specific areas identified for amine-based systems include:

- reduction of regeneration energy through development of a solvent or mixture of solvents with a lower reaction energy, and/or the use of a low value heat source to provide the required energy. MEA-based absorbent solutions generally require regeneration energies of 3–4 GJ/t of CO₂. European projects such as CASTOR aim to reduce this to 2 GJ/t ;
- development of advanced amines/mixtures with lower regeneration temperature;
- development of amines with a higher CO₂ loading that could be applied at a higher concentration to reduce pump requirements and equipment size;
- development of amines/blends with low loss into the flue gas or CO₂ stream. Also for degradation products;
- development of amines/blends and processes less sensitive to high temperature, SO_x, NO_x, and oxygen. Development of capture processes that can efficiently co-capture impurities of greater concentration (such as SO₂);
- development and application of advanced novel sterically-hindered amine solvents;
- deployment of combinations of membrane technology and solvent absorption;
- development of modified tower packing to reduce pressure drop and increase contacting;
- increased heat integration to reduce energy requirements;
- development of novel inhibitors – advanced additives to reduce corrosion and allow higher amine concentrations;
- development of more effective contacting surfaces in order to reduce size of equipment.

Many of the above points refer directly to the solvent itself. However, there are also significant opportunities for process enhancement through improved integration between the capture system and the host power plant. Potential areas identified include (VGB, 2004; Song and others, 2010):

- improved integration between reboiler and reclaimer and IP steam extraction;
- use of heat from CO₂ compression intercooling for feedwater pre-heating (although the impact may be limited);
- finding integration possibilities for use of heat from flue gas cooler, lean amine solution cooler, reflux condenser and CO₂ dryer (for instance, district heating or feed water preheating);

-
- design integration of steam cycle and CO₂ absorber-desorber process;
 - total plant re-optimisation involving the boiler, turbine, air quality control system, and CCS system;
 - investigation of possibilities for cost reductions through economy of scale.

Potentially, there are a number of ways to reduce the energy consumption in an amine-based CO₂ capture process using alternative, novel flow schemes rather than those currently being considered or deployed. A number of these have been proposed by different technology developers such as Fluor. To date, little has been published on the effectiveness of such flow schemes or their economic performance. However, recent studies and modelling have examined the possible application of a 'split-stream' configuration whereby a partly regenerated (semi-lean) amine solution is pumped from the middle of the stripper to the middle of the absorption column, and a completely regenerated (lean) amine is sent to the top. The regenerated amine solution from the desorber bottom is pressure reduced and lead to a flash tank (lean amine flash). The liquid from the flash tank is the lean amine stream which is recirculated back to the absorber. The vapour from the flash tank is compressed and returned to the bottom of the desorber. Simulations suggest that heat consumption for CO₂ capture could be reduced from 4.2 to ~2.5 GJ/t using a combination of vapour recompression and a split-stream configuration (Øi, 2011). Although heat requirements are reduced, greater work is required for vapour recompression. However, overall, there appears to be some benefit (Ploumen, 2012). It is not yet clear if these promising concepts will translate into pilot plant studies.

Although specific RD&D aims vary with the particular technology variant and developer, as noted, the overarching goal of many initiatives is focused firmly on minimising the energy penalty. Overall, where liquid solvents such as amines are used, they need to have a lower energy requirement for regeneration, be non-toxic, and have minimal environmental impact. Furthermore, they need to be robust in the presence of flue gas impurities and have a low degradation rate. In order to decrease capital and operating costs, further technological development is also necessary on plant components such as gas/liquid contactors. In the longer term, parallel to further developments of liquid sorbent-based capture systems, there is the need for the additional development and deployment of novel regeneration procedures. Potentially, some of these could provide significant advantages. However, many remain at early stages in their development. These candidate systems include adsorption by solid sorbents and high temperature carbonate looping cycles, membrane separation, cryogenic separation and use of biotechnology (ZEP, 2010a).

If, in the future, amine-based scrubbing systems are deployed widely on a large scale, there are several issues (some non-technical) that may require addressing. These are considered in the following sections.

3.4.1 Commercial supply of specialised amines

Potentially, the widespread industrial scale take-up of some types of amines and other solvents for CO₂ capture could provoke problems of supply; the total volume of solvent required could be considerable. With the aims of decreasing capture costs and energy penalties, a growing number of specialised solvents and blends are being developed and tested. At the moment, because volumes required are generally limited, supply is not an issue. However, in the longer term, consideration may need to be given to continued supply and competitive pricing of some of the variants being taken forward for utility-type operations.

Thus, the large-scale use of patented or proprietary solvents may present challenges; there may be patented features involved. Furthermore, for more exotic or rare solvents, less operational information is available (Owens and others, 2011). For large-scale extended deployment, consideration will need to be given to such issues. It may be more practical and cost-effective for a utility to opt for a readily-available, more conventional solvent of lower efficiency, than to use one of greater efficiency but much higher cost, one that may only be available from a single supplier.

The adoption of conventional amines may provide some advantages such as a proven track record, known operational behaviour, and multiple suppliers. Studies suggest that in the case of MEA, in the period up to 2020, supply would be adequate for a reasonably large degree of deployment. However, beyond this time, widespread deployment could begin impacting availability on the market (Miller and Zhou, 2011). Where more specialised amines were selected, the ease and cost of large-scale manufacture will require factoring in. Development of new manufacturing facilities could be a lengthy and expensive process.

3.4.2 Possible environmental impacts

As interest in the use of amine-based capture systems has increased significantly in recent years, scrutiny of possible environmental impacts has increased. It is well known that under some circumstances, amines can represent a health risk (Stoever, 2012). However, where amines are used for CO₂ capture, there appears to be a lack of knowledge on such risks, hence further research is required to fully explore this area. Some is under way; for instance, CSIRO has been commissioned by the Global CCS Institute to characterise the atmospheric emissions from a PCC process operating on a flue gas from a coal-fired power plant (*Assessing atmospheric emissions from amine-based CO₂ PCC process and their potential impacts on the environment – A Case Study*). From the data generated, the emission profiles and fate of the selected compounds when released to the atmosphere will be determined. The project outcomes are intended to support permitting and regulatory authorities in considering PCC demonstration project proposals. The project comprises the following activities:

- identify and quantify the types of emissions expected from the deployment of PCC processes using a selected amine solvent;
- assess the fate of compounds emitted to the atmosphere;
- assess the impacts of the selected emissions on local and regional air quality including the spatial extent of potential odour releases;
- discuss a possible framework that may be used by regulatory agencies for operational permitting approval of the plant.

Amine emissions may result from the baseline volatility of the compound and also from entrainment of liquid in the treated gas. Possible reaction products may exit the absorber either as volatile gases or mechanically entrained droplets. During operation, a small amount of the solvent (and solvent degradation products) will be released through the stack together with the cleaned flue gas. The IEA GHG R&D Programme suggests that in the case of a 400 MWe CCGT plant, a solvent slip of 1 ppm in the flue gas will add up to about 40 t/y. Potentially, this release could have a negative environmental impact both directly or indirectly through subsequent solvent degradation in the atmosphere into other substances. Thus, the expected emissions of amines, additives and their degradation products with the flue gas and waste product streams may pose an issue for the deployment of full-scale CO₂ post-combustion capture based on amines.

Environmental issues remain a focus for study, and various organisations are actively investigating potential risks and developing solutions. Areas highlighted include the need to quantify the amount and composition of solvent and degradation products in the cleaned flue gas, to understand the atmospheric fate and degradation of these substances, and to assess the final impact on the environment. Clearly, where necessary, it will also be important to develop technical solutions for their control. To date, the characteristics and impacts of used solvents and their degradation products are not fully understood (IEA GHG, 2010).

So far, relatively few studies have been undertaken to quantify the levels of amines and their degradation products that might be expected from commercial scale CO₂ capture plants, although investigations continue to be undertaken by different technology developers and vendors. For instance, a major screening study was undertaken by Knudsen and others (2009) which examined some of the commonest amines (MEA, AMP, MDEA, and piperazine), as well as the formation of toxic

compounds such as aldehydes, nitrosamines, nitramines and amides that may be formed by the reaction of amines with oxidised nitrogen compounds and/or photo-oxidation. The study was conducted to improve the understanding of atmospheric amine chemistry and to evaluate if the emissions caused by CO₂ capture in this manner pose a risk to human health and the natural environment. The work concluded that:

- amines themselves probably pose little risk to human health and the environment. However, amine emissions will contribute to the nitrogen load and potentially to eutrophication of sensitive terrestrial ecosystems;
- various compounds that may be formed from amines and by photo-oxidation in the atmosphere pose a potential risk to health and the environment. The main products may be nitrosamines, nitramines, aldehydes, and amides. Of particular concern are nitrosamines, which can be toxic and carcinogenic at extremely low levels. Nitramines are also of concern as they are suspected to be carcinogenic, although considerably less potent than nitrosamines. The suggested longer lifetime in the atmosphere may lead to higher exposure values;
- atmospheric dispersion models have shown that amine emissions can impact at both local and regional scales; modelling also indicates that amines lower the surface tension of water droplets that, under appropriate climatic conditions, could be a trigger for rain with the potential of impacting on the local environment;
- results from a ‘worst case’ study of emissions from a generic full-scale amine plant (with environmental conditions representing the west coast of Norway) showed that the predicted concentrations of suggested photo-oxidation compounds are at the same level of magnitude as the proposed ‘safety limits’, implying that risks to human health and the natural environment cannot be ruled out.

Various recommendations were made for improved qualitative and quantitative information for the compounds that may be involved, especially with regard to chemical pathways, chemical mass fluxes, dispersion, concentration, deposition, and the relative quantification of toxicity and other potential effects. Toxicity data so far available suggest that environmental and health risks represented by amines in CO₂ capture are ‘manageable’, and probably should not be a reason to inhibit or slow down the wide-scale deployment of CCS. However, greater effort is required to identify gaps in the knowledge and develop proper risk management strategies (Shao and Stangeland, 2009). It is suggested that these efforts should include:

- filling of knowledge gaps – in particular, determination of the atmospheric degradation paths, precise degradation yields, and degradation products’ lifetime in the atmosphere; also, determination of human toxicity exposure limits;
- develop amines with low environmental impact – continuation of ongoing research to develop new or improved amines, or mixtures of amines, with lower energy requirements, lower emissions and thereby lesser degradation products;
- develop amine capture plants with minimum emissions to air – various technology suppliers of such technologies (such as Alstom and MHI) are investigating various plant designs that could reduce emissions to air;
- ensure sound amine waste handling – determine how amine waste and degradation products can be turned into harmless materials. It will also be important to ensure that adequate waste handling capacity is available to handle expected volumes of wastes (*see* Section 3.4.3);
- develop alternatives to amines – further research to find alternatives to amines that could demonstrate better performance and lower CO₂ capture cost;
- establish proper regulations – once the knowledge gaps on the environmental and health impacts of amines have been filled, it will be necessary to implement regulations to ensure that CO₂ capture plants are designed and operated without negative environmental impacts;
- use CCS demonstration programmes to address risks associated with amines – demonstration projects that are based on amine absorption should include research activities aimed at providing data on associated environmental impacts.

Examination of possible environmental impacts is continuing with studies being undertaken by

various commercial technology developers. For instance, as part of their *Advanced Amine Process*, studies undertaken by Alstom Power and the Dow Chemical Company are focusing on potential environmental impacts on the environment with treated flue gas that is vented directly to atmosphere. The quantification and reduction of such emissions is being examined; minimisation of amine emissions is viewed as critical for both environmental and operational purposes. In order to gain public acceptance, it will be necessary for a particular plant to demonstrate that it can meet any amine emission limits in place. Furthermore, from an operational standpoint, amine losses in the treated gas will increase operating expenses related to solvent make-up and minimising such losses will help control the overall cost of the carbon capture process.

Alstom/Dow suggest that in order to minimise emissions, control strategies to reduce the amine content of treated flue gas will probably need to be incorporated in all commercial CCS facilities. The most common first approach to emissions control is likely to be the incorporation of a water wash section at the top of the absorber to remove amine and ammonia from the flue gas. The companies are continuing their examination of this area, with particular emphasis on their own family of proprietary UCARSOL solvents (Klinkera and others, 2011).

Other studies have been undertaken and emission control systems developed by MHI. In the 1990s, MHI's control technology was developed and commercialised. This focused on improvements to demister and packing systems. However, RD&D efforts are continuing, with pilot scale studies aimed at further development of the *MHI Zero Amine Emission System*. Monitoring has been carried out on a commercial plant in Japan to measure emissions of amine, degraded amine, ammonia, formaldehyde, acetaldehyde, carbonic acid and nitrosamines. So far, through process optimisation, no amine has been detected during pilot studies; only <0.2 ppm of degraded amine (as vapour) was detected. In 2003, MHI introduced an improved proprietary washing system that has since been applied to commercial units. With a view to full commercialisation, the technology will be demonstrated at larger scale on the Southern Company's Plant Barry project in the USA. Future RD&D activities will continue with the development of the Zero Amine Emission System. Environmental effects resulting from the photogenic reaction of amines released to air will also be evaluated. A 'worst case' study will be undertaken, with particular focus on the fate and impacts of nitrosamines (Kamijo, 2010).

Fluor also has a goal of minimising stack amine emissions from plants equipped with its Econamine FG+ technology and has been actively developing techniques to minimise such emissions. As part of this programme, the company has developed an advanced scrubbing system, whereby the solvent concentration in the vent is reduced to ~0.1–0.2 ppm. This was trialled on the commercial gas-fired Bellingham power plant in the USA, where a programme monitoring solvent emissions in the flue gas vent was undertaken. It was found that the solvent concentration in the absorber vent was less than 1 ppm (v/v). It was considered that systems with lower amine emissions can be designed, but would require a small increase in operating costs (Reddy, 2010). The amine emission control process and equipment is being tested at a 5 MW scale at E.ON's coal-fired Wilhelmshaven power plant in Germany.

3.4.3 By-product/waste disposal

Potentially, there may be environmental issues associated with the disposal of any by-products, such as heat stable salts, generated by different types of capture system. In some cases, operational experience has already led to the development of technological solutions. For instance, in the case of Tenaska's forthcoming Trailblazer project in the USA, Fluor's Econamine FG+ capture system has been designed so that no solid wastes will be produced. However, it will not be entirely waste-free. As with some competing systems, the Econamine process remains sensitive to incoming SO₂ in the flue gas, and any not removed by the scrubbing system can react with the EFG+ solvent and form heat stable salts. These can accumulate in the circulating solvent and lead to further solvent degradation and reduced process performance. To prevent this, the EFG+ process includes a semi-continuous

solvent reclaimer in which a slipstream of hot lean solvent is treated with sodium hydroxide. This reacts with the salts, frees up the solvent and forms non-volatile sodium salts. Most of the solvent is recovered and returned to the process. However, a small amount of solvent containing the sodium salts (reclaimer effluent waste) will be removed from the process (Christensen and Dysert, 2012).

Reclaimer effluent forms the main waste stream from this type of process. The amine reclaimer is the section of the process that separates or reclaims usable amine from its degradation products. The stream comprises water, amines, amine degradation products, corrosion products and other chemicals. The levels of amines and degradation products will vary and depends on the type of amine used and the nature of the flue gas being treated. Depending on the specific circumstances, a CO₂ capture plant with a capacity of 1 Mt/y is expected to produce between 300 and 3000 t/y of amine waste, although in most cases, the volume is expected to be less than 1000 t/y (Shao and Stangeland, 2009). Amine waste is classified as hazardous and must be handled in accordance with the appropriate regulations. It will usually require on-site treatment or, as in the case of the Trailblazer project, disposal via a permitted waste disposal contractor. There will clearly be a cost element involved.

With such effluent streams, the flow and more importantly, composition, will depend on the particular solvent or reagent used in the process (Owens and others, 2011). There are many different solvents, reagents and combinations available and the number continues to grow. These can include primary amines, secondary amines, complex (tertiary) amines, and other amine-based compounds. The growing number of formulations may produce a variety of by-products that will require separation, handling and disposal. This raises questions of toxicity and cost of disposal. It may be that disposal costs are much higher for by-products produced from some of the unique and patented 'designer' amine-based solvents or reagents, compared to simpler (but less efficient) equivalents. In general, the more complex the solvent, the more complicated the environmental signature of the process will be.

Some characterisation and impact studies have been carried out with regard to stack emissions, degradation, and toxicity. However, as new solvents and reagents are introduced, additional studies will be needed. It is acknowledged that reaction products present in stack emissions may not have been characterised as thoroughly as the solvent itself (Owens and others, 2011). To date, it appears that only limited consideration has been given to how to deal with by-products; this may prove to be of some importance, especially where a particular system has the potential of being deployed on a large scale. When evaluating a new solvent, consideration should be given to its disposal and any possible associated environmental impacts (Miller and Zhou, 2011). In most cases, it is not clear if this is always the case.

4 Amino acid salts

Aqueous solutions of amino acid salts can be used to capture CO₂ from flue gases, and several variants are being developed (mainly by Siemens, BASF and TNO) on the basis that they appear to offer a number of advantages over conventional amine-based scrubbing. Siemens is currently developing and testing a proprietary system known as *POSTCAP*. This is claimed to have a number of important advantages over conventional amines that include:

- minimal environmental impact as the solvent is biodegradable and has negligible vapour pressure;
- near-zero solvent emissions in cleaned flue gas and CO₂ streams;
- the solvent is easy to handle and non-toxic and exhibits low solvent degradation with O₂ in flue gas, hence reduced solvent refill is required;
- the process has low energy demand for solvent regeneration;
- there is the possibility of operating the process under different temperature and pressure conditions;
- it is possible to provide an enhanced process configuration for optimal integration into a power plant. Rapid installation and commissioning is expected.

The main components of the *POSTCAP* system comprise a flue gas cooler, an absorption and desorption column, heat exchangers, desorber top condenser, and steam-driven reboiler. CO₂ is captured using an amino acid solvent whose low absorption enthalpy and near-zero vapour pressure is claimed to make use economical and environmentally friendly. The technology has been designed and is being promoted for both new coal-fired power plants and for retrofitting to existing units. To date, pilot-scale developments have been used to validate the technology with a view to scaling-up to full-scale demonstration. These programmes have addressed issues such as the impact of the capture process on overall plant energy efficiency, the suitability of construction materials, and solvent stability and tolerance to trace compounds such as SO_x and NO_x. It has also provided insights into potential operating conditions.

4.1 Projects

The pilot scale studies undertaken so far suggest that the *POSTCAP* process could be effective at full commercial scale; CO₂ capture rates in excess of 90% are predicted. Several larger-scale projects are under way or planned. These are reviewed below.

Staudinger Unit 5, Germany

This 510 MW unit forms part of E.ON's hard coal-fired Staudinger power station. CO₂ is being captured under real conditions from the unit's flue gas via a slipstream and fed to a pilot capture facility, built by Siemens. Commissioning began in August 2009. Funding is being provided by E.ON and the Federal Ministry of Economics and Technology (BMWi). The plant is now treating 140 m³/h (TRL-6) of flue gas; this encompasses conventional cleaning (NO_x removal using primary measures, SCR, particulate clean-up by ESP, and SO₂ removal by means of a limestone FGD). The process is being validated under varying power plant operational requirements. Major aims (Jockenhövel and Schneider, 2010) of the test programme include examination of:

- heat and mass balance;
- energy demand and capture rate;
- solvent stability and prevention of crystallisation;
- qualification of materials;
- environmental impact, to prove low emission levels;
- analysis and evaluation of the operating behaviour of the process design under part-load and maximum load change gradients, start-up and shut-down.

Carbon capture using the amino acid salt solvent started in September 2009. The period of operation was scheduled to last for around sixteen months and by March 2011 the plant had operated for more than 4000 hours. Data gathered from the programme is helping confirm the suitability of the capture solvent; for example, its stability and suitability for CO₂ capture. Plant availability was as expected, and CO₂ capture rates exceeded 90%. The CO₂ loading of the amino acid salt reached high levels (Jockenhövel and Schneider, 2010). Reportedly, operation confirmed solvent emissions rates were practically zero. Solvent degradation was less than 1%/y, hence refill requirements were low. Corrosion tests confirmed that standard materials of construction could be used without problem, helping to minimise process costs. Overall energy consumption was claimed to be significantly lower than comparable conventional processes (Carbon Capture Journal, 2010). To date, testing suggests that the amino acid solvent is (Fout, 2011):

- less corrosive than MEA;
- has lower volatility than MEA;
- has a lower regeneration energy requirement than MEA (2.64 GJ/t CO₂ cf 4.25);
- has a capacity similar to hindered amine; it is moderately better than MHI's hindered amine.

Big Bend power plant, USA

The experience accumulated on the Staudinger pilot plant is providing data for the scaling up of the technology for a larger project being built at Tampa Electric's 1892 MW Big Bend power plant in Florida. The project also involves the US DOE NETL and Siemens. The 2.5 MWe (TRL-6) slipstream pilot plant has been installed downstream of an existing wet FGD system. There are a number of major objectives that the project aims to address:

- to demonstrate POSTCAP technology and achieve 90% CO₂ removal; confirmation that the technology can reach these removal levels under these conditions;
- to achieve a cost of electricity increase of no more than ~35%;
- to demonstrate the scalability and feasibility of progressing POSTCAP technology to full-scale commercial application (~550 MW) on coal-fired power plants and to full-scale commercial application for industrial sources of CO₂ emissions;
- to prove scalability and feasibility of the technology.

The project kicked-off in October 2010 and comprises three main phases. Phase 1 (October 2010 -July 2011) encompassed process design; Phase 2 (August 2011 – August 2012) will cover plant procurement and erection; and Phase 3 (September 2012 – July 2013) will be the operation and testing phase (Lang, 2011; Schneider and Schramm, 2011).

Longview power project, USA

During 2010, Longview Power selected POSTCAP technology as the basis for a study analysing its suitability for application on a new 695 MW supercritical (SC) power plant being built in West Virginia. The study included process design activities focused on the potential application of POSTCAP technology to the plant. This new power plant incorporates Siemens advanced air quality control system and will therefore be in a unique position to optimise this to accommodate the POSTCAP technology. The power plant was handed over to the operator in December 2011.

Hazelwood power plant, Australia

This pilot plant treats a flue gas slipstream from International Power's 1600 MW brown coal fired Hazelwood power plant (*see* Figure 12). The flue gas has a CO₂ content of ~13%. During Phase I of the project, the facility captured up to 25 tCO₂/d, although it has the potential to capture up to 50 t/d. Currently, the plant is capturing ~15 ktCO₂/y (TRL-6) of ~95% purity (ZEP, 2011). This equates to 0.1% of the station's total CO₂ emissions. The capture system uses the BASF solvent *PuraTreat*, a high-performance amino acid salt formulation used for the selective removal of H₂S and CO₂. Potentially, the capture plant could also be operated using alternative solvents such as generic amines and carbonate solvents (Dreher and others, 2010). Much of the CO₂ captured will be used to neutralise ash water, producing calcium carbonate and effectively storing the CO₂.



Figure 12 Amino acid-based pilot capture plant at International Power's Hazelwood power station in Australia (photograph courtesy of CO2CRC)

Organisations involved in the programme include International Power Australia, Siemens, Process Group, and CO2CRC. The plant has been funded by International Power with support from the Federal Government's Low Emission Technology Development Fund (LETDF) and the Victorian Government's Energy Technology Innovation Strategy Large Scale Demonstration Plant fund (ETIS LSDP).

The main aims of the project include the demonstration and operation of the capture technology on a commercial-scale coal-fired power plant. It is anticipated that data produced by the programme will provide the basis for subsequent R&D into post-combustion capture, in association with CO2CRC (International Power, nd). A number of possible routes are being examined with a view to improving the operation and economics of the CO₂ capture stage as well as scaling up the process. To reduce associated capital and operating costs, a number of concepts are being considered. These include modifications to the absorber and regenerator vessels, the use of modularised pre-built (absorber/regenerator) structures, and plant turn-down via multiple capture units. Other

cost-reducing possibilities include the adoption of a novel froth absorber, and the greater use of concrete to reduce construction costs. Full opportunity of savings identified will be implemented on any future large-scale CCS projects. Other areas that could enhance plant operations include improved vessel design and construction and improved heat integration with the host power plant (Dugan, 2010).

Potentially, overall plant size could be reduced by the adoption of advanced gas absorption technology currently being evaluated, or through the use of a novel micro-froth matrix mass transfer unit. This could lead to significantly smaller plant components. The system would also allow plant operation with precipitating solvents that could significantly increase solvent loading.

Maasvlakte, The Netherlands – CATO CO₂ Catcher project

In 2008, a pilot-scale project, located at the coal-fired Maasvlakte power plant in Rotterdam began operations as part of the CATO programme (Davidson, 2007). This has the aim of testing novel CO₂ gas scrubbing processes under real industrial conditions. The project is being developed jointly between TNO and E.ON Benelux. The pilot plant is connected to the stack of Unit 2 of the power plant, after desulphurisation. As part of the campaign, TNO is developing the *CORAL* family of absorption solvents based on amino acid salts.

Results from pilot plant activities have confirmed the potential of some *CORAL* solvent compositions. In more than 3000 hours of operation, *CORAL* XPT has been shown to be very stable under industrial conditions, with degradation losses of less than 0.15 kgCO₂/t. Furthermore, it appears that regeneration energy required is relatively low, compared to some competing capture systems (Goetheer and Nell, 2009).

The CATO project has also examined the use of amino acids as part of the so-called DECAB process.

Table 13 Project survey – major coal-fired, amino acid-based post-combustion CO ₂ capture activities						
Country	Project	Lead organisation(s)	Plant/capture facility, MW	CO ₂ fate	Proposed start-up	Comment/status
Australia	Hazelwood	International Power, Alstom, Process Group, CO2CRC	1600	Around 15–25 t/d	Capture pilot started up in 2009	Brown coal fired. Testing coal drying, solvents, absorbents, membranes, and equipment. Operating with BASF PuraTreat amino acid (2011)
Germany	Staudinger	E.ON, Siemens, BMWi	510		2009-12	Siemens POSTCAP system. 1 MW pilot programme. Mainly solvent testing
Netherlands	Maasvlakte	E.ON Benelux, TNO, Siemens	1040	Up to 250 kg/h		Part of CATO project. Testing of TNO CORAL and other solvents
USA	Big Bend, Florida	Tampa Electric, Siemens	1892		2013	2.5 MWe slipstream project. Siemens POSTCAP system
	Longview	Longview Power, Siemens	695		New SC power plant unit start-up in 2011	Study undertaken for use of Siemens POSTCAP technology

In this patented absorption process, the amino acid is neutralised with potassium hydroxide. During CO₂ capture, precipitates are formed. It is claimed that the technology has the potential to substantially decrease investment costs and process energy requirements. Through the use of the precipitation technique, high cyclic CO₂ loadings can be achieved, resulting in potentially cost-effective process designs (Brouwer and others, 2005). It is suggested that the costs per tonne of CO₂ captured by the DECAB process could be half that of an MEA process. However, this requires confirmation. A summary of the main amino acid-based capture projects is presented in Table 13.

4.2 Future RD&D focus and challenges – amino acids

Aqueous solutions of salts of amino acids appear to provide an effective alternative to amines for CO₂ capture from some flue gases. Some of those being developed and tested (by for instance, the Dutch CATO programme) are showing good oxygen resistance, lower binding energies, and fast reaction kinetics. Using a precipitation technique, high cyclic loadings can be achieved, resulting in potentially cost-effective process designs. However, future RD&D efforts are required to confirm fully the potential of amino acid-based solvents and processes. Areas identified that would benefit from further development include:

- development of improved liquid-gas contacting (in spray columns) with formation of precipitates;
- development of novel amino-acid salts with favourable precipitation characteristics;
- further assessment of impacts of SO₂ and high oxygen content in flue gases;

-
- development of more detailed equilibrium, kinetic and transport data for precipitating solvents;
 - validation of the technology in large-scale pilot plant (Brouwer and others, 2006);
 - development of solvents with improved properties;
 - development of novel process concepts aimed at reducing further energy requirements;
 - confirmation of system operation that encompasses frequent load changes (Lang, 2011).

Some of the above are being addressed through the various pilot-scale projects already noted. However, there may also be non-technical areas that will require addressing. For instance, commercial solvent suppliers may be required, capable of providing solvents on a large scale

5 Aqueous ammonia-based systems

Ammonia-based scrubbing operates in a similar manner to amine-based systems. So-called aqueous ammonia systems are, in reality, based on ammonium carbonate solution that reacts with CO₂ to form the bicarbonate. Advantageously, this reaction has a significantly lower heat of reaction than amine-based systems; provided that the absorption/desorption cycle can be limited to this mechanism, energy savings can be achieved. Other advantages claimed over amines include the potential for higher CO₂ capacity, lack of degradation during absorption/regeneration, better tolerance to oxygen in the flue gas, lower cost, and potential for regeneration at high pressure. The advantages and disadvantages of the technology are summarised in Table 14.

Studies have confirmed that the CO₂ transfer capacities of aqueous ammonia solutions can be higher than those of MEA solutions. In addition, the energy requirement for liquid mass circulation of ammonia solution is around half that required for MEA solution for an equal weight of CO₂ carried. The thermal energy required to regenerate CO₂ from the rich solution is substantially less for an ammonia solution than for MEA. Absorbent degradation and potential corrosion problems are also less. Potential areas of concern are ammonia loss and the formation of precipitates (Davidson, 2007; Spitznogle, 2011).

As a result of ammonia's higher volatility (compared to MEA), flue gas must be cooled typically to the 16–27°C range to enhance the CO₂ absorptivity of the ammonia compounds and to minimise ammonia vapour emissions during the absorption step. Additionally, as regeneration takes place at elevated temperatures, there may be an issue of ammonia loss.

Advantages	Disadvantages
Lower heat of regeneration than amines, reducing the energy consumption associated with solution regeneration	Ammonium bicarbonate decomposes at 60°C, so temperatures in the absorber must be kept below this
Higher net CO ₂ transfer than amines	Ammonia is more volatile than, for instance, MEA, and can produce an ammonia slip into the exit gas
Higher loading capacity than amines	Because of lower reaction rate and CO ₂ loading than amines, may require a larger absorber
Fewer corrosion issues than amines	May be issues of precipitation
Does not degrade in a flue gas environment, minimising absorbent make-up	Cooling energy required for Chilled Ammonia Process (chilled water)
Lower cost than amines	
Stripping steam not required	
More tolerant to pollutants such as SO ₂	
Offers possibility of multi-pollutant control (for example ECO ₂ system)	

5.1 Alstom chilled ammonia capture process (CAP)

The chilled ammonia process is being developed and promoted by Alstom. It uses the same

ammonium carbonate/bicarbonate absorption chemistry as the aqueous system, although here the system circulates a slurry of aqueous salts and solid ammonium bicarbonate to capture CO₂.

The process uses the changes in chemical equilibrium of ammonia, ammonium carbonate, and ammonium bicarbonate, with change in temperature to capture and release CO₂ captured from the flue gas stream. Operation is carried out at near freezing temperatures (between 0°C and 10°C) and the flue gas is cooled prior to absorption using chilled water and a series of direct contact coolers. Cooling of the flue gas to these low temperatures minimises ammonia losses. It is reported that for a supercritical PCC power plant equipped with the chilled ammonia process, the CO₂ avoided cost would be 19.7 US\$/tCO₂, compared with US\$51.1 for the equivalent MEA process. The power reduction for a plant equipped with chilled ammonia scrubbing would only be ~10% (Davidson, 2007).

Advantages claimed for the process include the low cost of the solvent, and its resistance to degradation at elevated temperature and with exposure to SO₂ and NO_x. In addition, the use of a higher stripping temperature allows the process to release CO₂ at a higher pressure than is possible with amine solvents. A possible disadvantage is that it requires a larger absorber as it has a relatively low reaction rate and CO₂ loading. Some efficiency is also lost to the chiller, needed to maintain reaction temperature.

Depending on the composition and design of a particular plant, it may be possible to generate a useful income stream. The flue gases from a typical wet FGD system can be delivered to the chilled ammonia process without any additional treatment. The by-product from a CAP facility is a liquid ammonium sulphate stream that can be used as a feedstock for chemical manufacture; for instance, the production of sulphate-based fertilisers (Getica CCS, 2011).



Figure 13 The Alstom chilled ammonia capture plant installed at We Energies Pleasant Prairie power plant in Wisconsin (photograph courtesy of We Energies)

Projects

Compared to amines, there are fewer projects under development; these are under way or have been completed in the USA, Europe and Australia. Data generated from these are contributing to the commercial scale-up of the technology. The current status of the various CAP projects are discussed below.

In the USA, the chilled ammonia process was demonstrated successfully on a 5 MW (TRL-6) slipstream project located at We Energies Pleasant Prairie power plant in Wisconsin (see Figure 13). Between 2008 and 2009, this operated for a total of 7700 hours. The test campaign confirmed the predicted performance of the system; a high level of CO₂ (~90%) was captured, confirming that the system could operate successfully under real power plant conditions. The plant was designed to capture >15 ktCO₂/y. During operation, there was very little ammonia loss, high CO₂ purity was achieved, and reliable system operation was demonstrated. The major achievements of the pilot programme included (Telikapalli and others, 2011):

- CO₂ product quality >99.5%;

- sustained regeneration at 2.1 MPa;
- residual flue gas NH₃ emissions <10 ppm;
- minimal solvent degradation;
- operational uptime of 66% through full run time;
- heat integration design limits identified;
- heat of regeneration reaction validated;
- mechanical inspection confirmed material selection;
- sustained operation through power plant transients.

Based on the Pleasant Prairie pilot plant's success, in 2009, a scaled-up slipstream project (20 MWe) (TRL-7) was installed at AEP's 1300 MW coal-fired Mountaineer Station in New Haven, West Virginia. Using data generated at Pleasant Prairie, a number of improvements were incorporated into the design of the New Haven plant. These included:

- adoption of a two absorber system to capture 75% of the flue gas CO₂, achieving the objective of 100 kt/y capture;
- improvements/simplification of the water wash system;
- improved configuration of the plant refrigeration system.

In 2011, Alstom Power announced the successful operation of the Mountaineer CCS validation project. The plant represented a successful ten-fold scale-up of previous field pilots such as Pleasant Prairie. Reportedly, the test programme achieved capture rates from 75% to 90% at CO₂ purity >99%. Energy penalties were within a few per cent of predictions from Alstom's process simulation model. Robust steady-state operation during all modes of power plant operation (including load changes) was achieved and availability of the CCS system was in excess of 90% (Alstom, 2011). There was general satisfaction with the plant's materials of construction although localised incidents of chemical attack are being investigated. No solvent degradation was detected after 15,000 hours of operation. Ammonia losses were below design values (Kozak and others, 2011). CO₂ captured was injected successfully into deep geologic formations beneath the Mountaineer plant. The plant operated up to June 2011.

The results provided confidence for scaling-up the technology further to capture 1.5 MtCO₂/y at Mountaineer. However, in July 2011, the proposed scaled-up project was placed on hold until such time that economic and policy conditions create a viable path forward. A second project was planned for AEP's 450 MW Northeastern Station in Oklahoma. Here, it was proposed that a slipstream project would treat around half of the station's output (~235 MWe). Around 1.5 MtCO₂/y was to be captured and stored on deep saline aquifers or used for EOR.

In **Canada**, the chilled ammonia process was to be deployed on a new 450 MW SC PCC unit at Capital Power's Keephills 3 station in Alberta. This new SC unit began commercial operations in September 2011. Organisations involved included TransAlta, TransCanada, Alstom, Capital Power and Enbridge. The new SC unit was to be retrofitted with the CCS system. This project (*Project Pioneer*) was expected to capture around 1 MtCO₂/y for storage in a saline formation and/or used for EOR. It was to capture 90% of the CO₂ from a flue gas slipstream, along with most of the SO₂ and particulates not removed by the plant's FGD process. Overall, around a third of the CO₂ produced by the unit was to be captured. The CAP capture plant was to be fully integrated with the power plant's steam cycle. On-site construction of the pilot plant was scheduled to begin in 2012 and the facility to become fully operational in 2015 (Telikapalli and others, 2011). The proposed timetable for this multi-phase project is shown in Table 15.

The key components of Project Pioneer were to comprise the pilot capture facility, plus appropriate pipelines. These were to direct captured CO₂ to a deep saline formation in the Wabamun Lake area. An evaluation drilling program was under way in 2011 to confirm the suitability of the geology of the formation. A second pipeline was also to be built to transport CO₂ to the primary EOR target, the Pembina oilfield, where the CO₂ was to be injected for EOR purposes.

Table 15 Schedule for development of Project Pioneer (Telikapalli and others, 2011)

Phase/timescale	Activities
Up to Q1-Q2 2012	Front end engineering and design
	Storage site evaluation
	Commercial development
	Environmental and permitting activities
	Public consultation
	Initial investment decision
Mid 2012 to Q1-Q2 2013	Detailed engineering and long lead procurement
	Completion of commercial development
	Completion of environmental and permitting activities
	Public consultation
	Final investment decision
Mid-2013 to mid-2015	Construction of carbon capture facility, pipelines and storage facilities
June to November 2015	Commissioning of carbon capture facility, pipelines and storage facilities
Late 2015 to 2025	Operation, optimisation and maintenance of carbon capture facility, pipelines and storage facilities

In late 2011, Project Pioneer was executing FEED for the capture facility, pipelines and storage sites, as well as undertaking associated commercial development, permitting and regulatory activities. Subject to regulatory approvals, market conditions, and internal project approvals, construction of the project was scheduled to begin in 2014, with commercial start-up in 2015. The project planned to continue commercial operations for ten years and may be extended further. At the end of 2011, the project was reported to be on time and on budget. Over 80% of the contracts for the project had been awarded. Tenders had also been granted for the piping, boilers and turbines. However, in April 2012, it was announced that Capital Power had abandoned the CCS project. Reportedly, the company had no buyers for the carbon dioxide and no way to credit from the plan. Following the conclusion of the FEED study, it was determined that the revenue from carbon sales and the price of emissions reduction technology were insufficient to move ahead with the project at this time.

In **Australia**, a joint venture between Delta Electricity and CSIRO saw the construction and operation of a CAP pilot capture plant at Munmorah. The unit was commissioned in 2008 and became operational in 2009. Goals included examination of system tolerance to NO_x and SO_x, ammonia loss, and process energy requirements. In operation, the pilot plant achieved capture rates in excess of 90%, producing a high purity CO₂ product (>98.5%). A high level of SO₂ removal was also achieved using ammonia wash water. The results of the pilot studies are being fed into a larger scale project announced in March 2010 (the Delta CCS demonstration project). Funding has been agreed for the first stage of the project that will demonstrate CO₂ capture using chilled ammonia, transport, and permanent geological storage (up to 100 kt/y in a saline aquifer) from a black coal fired power station.

Late in 2010, it was announced that Alstom's chilled ammonia process had been selected by **Romania's** Institute for Studies and Power Engineering as part of an integrated CCS demonstration proposed for the 330 MW Unit 6 of the lignite-fired base-load Turceni power plant (The Romanian Getica CCS Demonstration Project) (Sava, 2011). Unit 6 is currently being retrofitted and its operating lifetime extended; a wet FGD system is scheduled to be installed by 2012, with construction completed by 2013. Once the CO₂ capture plant is operational, it is estimated that around 1.5 Mt/y (TRL-8) of CO₂ will be captured (85% minimum), transported and stored in deep saline aquifers within a 50 km radius of the plant (Romanian CCS project, 2011). The capture plant will treat an

equivalent flue gas flow of 250 MWe of gross electrical output. The project's planned start-up of operation is December 2015.

A new tripartite company has been created to take the project forward, made up of three existing companies owned by the Romanian state as the majority shareholder. Each has expertise in specific areas of CO₂ capture, transport and storage:

- CE Turceni SA, an electricity generation company;
- SNTGN Transgaz SA, a natural gas transportation company;
- SNGN Romgaz SA, a natural gas extraction/storage company.

The feasibility study phase had been completed by the end of 2011 and the project was progressing towards the FEED and Appraisal phase. The consultant for the feasibility study was the Institute for Studies and Power Engineering (SC ISPE SA) together with Alstom Carbon Capture GmbH. Alstom chilled ammonia technology was selected on the basis of the promising data obtained from successful pilot operations at the US-based AEP Mountaineer project and elsewhere (Getica CCS, 2011; GCCSI, 2012a). The technology was considered to be one of the capture technologies furthest in development and closest to full commercialisation. The objective of this demonstration project is to further validate the CAP process under industrial scale conditions. Importantly, the chilled ammonia process has demonstrated stable operation at turndown conditions and offers the flexibility and ability to follow daily and weekly changes in plant load requirements without impact on the capture process (Getica CCS, 2011).

In September 2011, it was announced that Alstom and China Datang Corporation had signed a MoU to develop carbon capture demonstration projects in China. One of these will be located at the 1 GW Dongying coal-fired power plant in Shandong province. This will adopt either Alstom's chilled ammonia or advanced amine process. The project is scheduled to begin operations by 2015, with captured CO₂ being used for EOR (Alstom, 2011).

Although not coal-based, development work is also continuing at E.ON's oil-fired Karlshamn power plant in Germany.

5.2 Powerspan ECO2 ammonia-based capture process

The process is similar to that of some other CO₂ absorption processes in that CO₂ is absorbed in a solution through flue gas:solution contact, the solution is heated for regeneration, CO₂ is released, and the solution is cooled for reuse (McLarnon and Jones, 2008). Unlike the Alstom capture process, the ECO2 capture process does not first chill the ammonia. The unique feature of the ECO technology is claimed to be its ability to simultaneously remove SO₂, NO_x, PM_{2.5}, acid gases, Hg, and other metals from the flue gas of coal-fired plants. The multi-pollutant treatment takes place in three distinct steps. In a typical plant, the ECO (electro-catalytic oxidation) system is installed downstream of the existing ESP or fabric filter.

The technology uses an absorption column and thermal stripper and is interconnected with Powerspan's ECO multi-pollutant control system. CO₂ absorption into the ammonia-based solvent takes place at low temperature, similar to that of wet flue gas scrubbing systems. Initially, particulates are removed from the flue gas which is then directed upwards through the ECO2 wet scrubber. The ammonia scrubber removes unconverted SO₂, acid gases and HgCl₂. CO₂ capture takes place after the removal of NO_x and SO₂. Once the CO₂ has been captured, the ammonium bicarbonate solution formed is heated with steam to regenerate the ammonia which is then returned to the scrubbing process, and the CO₂ released. This is then compressed and sent for storage or utilisation. NO₂ from the flue gas combines with the SO₂ and ammonia to produce liquid ammonium sulphate, which can be used as a fertiliser.

Project survey

To date, a small number of projects have been proposed or are under way, mainly in North America. However, for a number of reasons, several are currently on hold.

Starting in December 2008, a 1 MW slipstream pilot project (from a 156 MW coal-fired unit) was operated from an existing 50 MW ECO demonstration installed at FirstEnergy's 541 MW **R E Burger Power Plant** in Ohio, USA (*see* Figure 14). A primary aim was to demonstrate the ability of the CO₂ capture process to be integrated with the ECO multi-pollutant control system and to confirm process design and cost estimates. The unit was originally intended to capture 20 tCO₂/d of (TRL-6) (90%



Figure 14 The R E Burger Power Plant in Ohio, USA, housed a demonstration of Powerspan's ECO2 ammonia-based capture process (photograph courtesy of FirstEnergy)

capture rate) although subsequent modifications increased this to >25 t/d (equivalent to 1.3 MW). During extended operations, the facility averaged >90% CO₂ capture from inlet gas that contained 11–12% CO₂. The product CO₂ was purified to meet industrial pipeline specifications. The pilot plant demonstrated successfully that it was capable of adapting to changing power plant conditions, an important step towards commercialisation. It ceased operations in December 2010. Reportedly, studies of process economics have since confirmed that the technology would be viable for both new build and retrofit situations. It was planned that, beginning in 2012, the technology would be scaled up to 120 MW and tested

at Basin Electric's Antelope Valley Station in North Dakota. This project was subsequently cancelled and the CO₂ capture component of the project taken over by HTC Purenergy. However, because of cost and timing issues, carbon capture activities at the site have been put on hold for an indefinite period.

A demonstration project was planned for a 125 MW slipstream from a 600 MW unit at NRG Energy's WA Parish Plant in Sugar Land, Texas. However Fluor's Econamine FG+ technology was later selected.

An independent review of the design, operation, and performance of the ECO2 technology operations at the Burger plant was subsequently carried out by WorleyParsons. It was concluded that the pilot facility had provided a sound basis for the full-scale application of the ECO2 system, and that the technology was ready for application in 200 MW or larger plants. For larger scale deployment, costs for CCS facilities based on the technology were determined to be at the lower end of previous estimates (Vazaios, 2010). A summary of coal-fired projects using ammonia-based CO₂ capture systems is given in Table 16.

5.3 Future RD&D focus and challenges – ammonia-based systems

Studies carried out by the US DOE/NETL and others suggest that post-combustion CO₂ capture using ammonia looks promising. If various engineering challenges can be fully overcome, there is the

Table 16 Project survey – major coal-fired, ammonia-based post-combustion CO ₂ capture projects							
Country	Project	Lead organisation(s)	Plant/capture facility, MW	CO ₂ fate	Proposed start-up	Comment/status	Estimated TRL
Australia	Munmorah pilot	Delta Electricity, CSIRO, Alstom		Pilot – 3000 t/y Demo – 100 kt/y Geo-storage	Pilot started up in 2009. Will operate until 2013	Alstom CAP technology. Pilot data feeding into proposed larger Delta CCS demo project – start-up 2015	6
							7
Canada	Keephills 3, Alberta (Project Pioneer)	TransAlta, Capital Power, Alstom	450	~1 Mt/y Saline aquifer and/or EOR	2015	Alstom CAP technology. But project cancelled in April 2012	8
Romania	Getica CCS demo, Turceni	CE Turceni SA, SNTGN Transgaz, SNTG Romgaz, Alstom	330	1.5 Mt/y. Saline aquifer	2015	Alstom CAP technology. 250 MWe equivalent slipstream	8
USA	Pleasant Prairie, Wisconsin	We Energy, Alstom	5 MW slip-stream	>15 kt/y	2008-09	Project completed. Alstom CAP technology	6
	Mountaineer, West Virginia	AEP, Alstom	20 MW slip-stream	100 kt/y	2009-11	Project completed. Alstom CAP technology	7
	R E Burger power plant, Ohio	PowerSpan	1.3 MWe	>25 t/d		PowerSpan ECO2 technology.	6
	Antelope Valley, North Dakota	PowerSpan	120 MWe		2012	Scaled up Burger technology. But project currently on hold	7

potential for the overall cost of an ammonia-based system to be significantly lower than an amine-based system. With further development, both the aqueous and chilled ammonia processes are considered to have the potential for better energy efficiency than amine-based systems. Although (compared to amines), the use of ammonia offers several advantages such as lower heat of regeneration and fewer corrosion issues, it is considered that there is still room for further improvements to be made to the technology. Several areas have been highlighted as having the potential to improve process economics and performance. These include:

- development of optimised/improved process configurations so as to increase CO₂ loading;
- improved cooling of the flue gas and absorber to maintain operating temperatures below 10°C, necessary for reducing ammonia slip, achieving high CO₂ capacities, and for ammonium carbonate/bicarbonate cycling;

- development and application of enhanced engineering techniques leading to reduced ammonia slip during absorption and regeneration and vapour losses during operation;
- achievement of 90+% removal efficiencies in a single stage;
- avoiding fouling of heat transfer and other equipment by ammonium bicarbonate deposition as a result of absorber operation with a saturated solution;
- development of systems capable of capturing multiple pollutants (CO₂, SO₂, NO_x, Hg) simultaneously, leading to reduced plant costs.

6 Oxyfuel combustion

This chapter reviews and summarises the major projects, proposals and RD&D activities under way aimed at the further development of oxyfuel combustion CO₂ capture.

Oxyfuel combustion is one of the three main routes being pursued towards cost-effective, technically-viable carbon capture (Figure 15). CO₂ is captured from flue gas by modification of the combustion process so that the gas generated contains a high concentration of CO₂. In the process, fuel is combusted in an atmosphere comprising oxygen (usually 95–99%) and recycled flue gas (RFG). Much of the nitrogen is eliminated from the process. Instead, CO₂ is recycled in a semi-closed cycle, serving as the working fluid (Luby and Susta, 2007). The use of oxygen and RFG maintains combustion conditions similar to that of a conventional air-fired configuration. This is necessary as materials of construction currently available are unable to withstand the high temperatures generated by burning coal in pure oxygen.

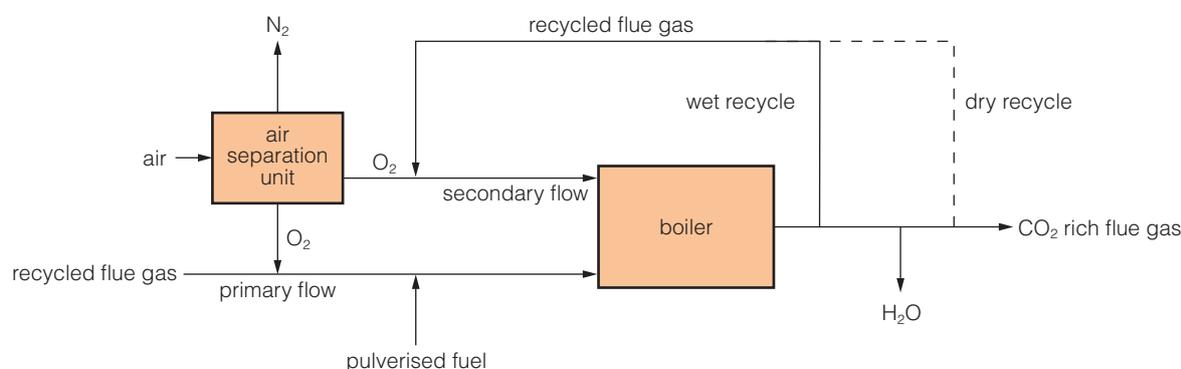


Figure 15 Schematic of oxyfuel combustion/CCS system

Oxyfuel can essentially produce a near-zero gaseous emission power plant (with only a small vent stream from the cryogenic purification unit). Oxyfuel combustion offers a number of advantages over some competing carbon capture technologies (Moorman, 2011):

- the boiler and air quality control system equipment utilise conventional designs, materials of construction and arrangements. These usually take the form of equipment combinations and processes that are well-known to industry users;
- oxyfuel systems will look and operate in a similar manner to a conventional power plant. Pilot-scale testing suggests only minimal impacts on boiler combustion and little change to thermal performance. Air quality control system performance is likely to be largely unchanged. There should be little change in the way major plant components operate (furnace and heating surfaces, coal pulverisers, FGD systems, ESP or baghouse, and basic plant operating controls);
- the oxyfuel process can utilise a wide variety of coals that include lignites, subbituminous and bituminous coals;
- compared to post-combustion, oxyfuel systems should be easier and less complex to repower or retrofit into an existing power plant;
- no new chemicals or waste streams are introduced into the plant process. Bottom ash, fly ash, and FGD waste streams remain largely unchanged;
- there is no major change to the plant water balance. For low rank fuels, there may be a positive water balance from condensation of water from the flue gas stream.

The main advantages and disadvantages of oxy-fuel combustion are summarised in Table 17.

A major advantage of the technology is that it produces a flue gas which comprises predominantly CO₂ (>80% vol) and water. The latter can be removed easily by condensation, allowing the remaining

Table 17 Advantages and disadvantages of oxyfuel combustion (GCSSI, 2012e; Moorman, 2011)	
Advantages	Challenges/barriers to implementation
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	Not possible to develop sub-scale oxy-combustion technology at existing power plants. Requires commitment of the whole power plant
Necessary extra equipment comprises mainly conventional rotating equipment and heat exchangers. The boiler and air quality control system equipment utilise conventional designs, materials of construction and arrangements, all well-established in industry	Energy penalty – power needed for ASU air compression 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 of same capacity without CO ₂ capture
Very low emissions of conventional pollutants usually achievable at relatively low cost	Currently, little geological or regulatory consensus on what CO ₂ purity levels will be needed for compression, transportation and storage. If purity requirements are lower, oxy-combustion costs could be reduced
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% capture	Air-fired combustion is commonly anticipated for start-up of oxy-combustion power plants. If a significant number of annual restarts are specified, additional flue gas quality controls may be required or provisions made to start up and shut down the unit only with oxy-firing and without venting significant amounts of flue gas
Current information suggests that oxy-combustion with CO ₂ capture should be competitive, or slightly more cost effective than pre- and post-combustion capture	Need to reduce CAPEX and OPEX, although this issue is common to all capture technologies
Should be easier and less complex to repower or retrofit into an existing power plant than post-combustion capture	Technology needs proving through the integrated operation on a larger scale and under different operating conditions (start-up, shutdown, load variations)
An oxyfuel power plant will largely look and operate in a similar way to a conventional power plant	Installation must be air tight to avoid air in-leakage. If over pressurised, there is the risk of CO ₂ leakage
Can utilise a wide variety of coals	
No on-site chemical operations are required. Waste streams largely unchanged	

CO₂ to be purified relatively inexpensively. Conditioning of the flue gas consists of drying the CO₂, removal of oxygen to prevent corrosion in the pipeline, and possibly removal of other contaminants and diluents such as nitrogen, SO₂, and NO_x. The cost of CO₂ capture in such a system should be lower than for a conventional PCC plant, as a result of the decreased flue gas volume and increased concentration of CO₂. However, at present, the cost of air separation (oxygen generation) and flue gas recirculation significantly reduces the economic benefit.

Oxyfuel technology is currently undergoing rapid advancement, with the development of a number of international pilot/demonstration projects under way. Industrial-scale testing of coal combustion and burners is also being conducted by several technology vendors (Wall and others, 2010). However, the technology holds potential for further development. For instance, ion-transport membranes (*see* Section 9) and other novel techniques for lower-cost O₂ production are being developed and are expected to be available within the next decade. These hold the potential for significant process cost

reduction. There will also be benefits for oxygen-blown IGCC technology which can use the ITM O₂ technology.

Oxyfuel combustion is considered suitable for application to both new-build power plants and retrofit situations. Essentially, the technology is an adaptation of existing components and sub-systems to a new application; most of the sub-systems already exist. Furthermore, test results from large pilot projects appear to be confirming the robustness of the technology. Oxyfuel combustion capability and CO₂ capture is technically straightforward when taken into account during the initial design of the power plant; only moderate modifications to the power plant would be required for the future conversion to oxyfuel combustion. Thus, for retrofitting, it appears technically possible to convert at least some non-capture-ready plants to oxyfuel combustion, although the performance would not be as good as that of a new high efficiency plant featuring an optimised oxyfuel CCS solution. However, this would be normal for retrofit scenarios and would also be the case with post-combustion (Oettinger, 2012a). By way of example is the Total Lacq project in France, where an existing 50-year-old boiler has been retrofitted with oxyfuel combustion technology. These are key reasons to consider oxy-combustion for capture-ready power plants.

Project survey

The GCSSI has identified four pilot-scale oxyfuel-based projects currently operating. Three of these are coal-based and one, natural gas (Total's Lacq project) (EPRI, 2012). The coal-based projects, plus those proposed or under development, are discussed below.

Asia-Pacific region

Callide Oxyfuel Project, Queensland, Australia

The Callide A power plant is near Biloela in central Queensland (Figure 16). It is being refurbished to operate as a 30 MWe oxyfuel (TRL-7) pilot plant. It will become the world's first power plant to be retrofitted with oxyfuel technology. The project aims to demonstrate that CO₂ capture, based on oxyfuel combustion, can be combined with carbon storage to significantly reduce emissions from a coal-fired power plant. The project encompasses refurbishment of the plant's boiler, retrofitting of oxyfuel technology, CO₂ compression and purification (75 t/d process plant from a 20% sidestream), and road transport and geological storage of around 30 t/d of liquid CO₂ (Santos, 2011).

Once completed, the plant's boiler (a Riley Dodds two-drum type, without reheater) will be capable of operating in both air and oxyfuel mode. When operating in the latter, coal will be burned in a mixed gas atmosphere comprising pure oxygen (98%) and recirculated flue gas. Boiler inlet oxygen concentration will be 27%.



Figure 16 The Callide power plant in Australia (photograph courtesy of CS Energy)

The change from air to oxyfiring will be conducted between 80% and 100% maximum continuous rating (MCR); there will be no requirement for oxy mode under start/stop or low load conditions. The overall plant operating targets include a ramp up rate of 5%/h, a ramp down rate of 1%/m (both in oxy mode), and a minimum load (turndown) of 80%. Switching between air and oxy modes will take around 60 minutes (Spero and others, 2011). Combustion mode

change is one of the most important processes in oxyfuel boiler operation. At Callide, boiler start-up and shut-down will be conducted with air combustion using fuel oil. After achieving >80% load in air combustion with coal, operations will be switched to oxyfuel conditions. The boiler steam conditions will be a pressure of 4.1 MPa, temperature of 460°C, and a flow rate of 136 t/h. The fuel used will be mainly Callide coal, sourced locally; this is characterised by high ash, high moisture and low sulphur content. However, other coals will also be evaluated (Gotoua and others, 2011).

The Callide project comprises three main stages. Stage 1 covers the boiler retrofit and CO₂ capture; Stage 2 is CO₂ road transport and geological storage; and Stage 3 will encompass the project's conclusions. The total demonstration period is scheduled to be about seven years. The main goals are to:

- demonstrate a complete and integrated process of oxyfuel combustion of pulverised coal within a national electricity market facility, incorporating oxygen production, oxyfuel combustion, CO₂ processing and liquefaction, plus CO₂ transport and geological storage;
- obtain detailed engineering design, cost data, and operational experience to underpin the commercial development and deployment of new and retrofit oxyfuel boiler applications for electricity generation;
- obtain detailed geotechnical design and cost data and operational experience to support the development of geological CO₂ storage projects (Gotoua and others, 2011).

The Callide Oxyfuel Project is a joint venture between Australian and Japanese partners that include CS Energy, the Australian Coal Association, Xstrata Coal, Schlumberger, and Japanese participants, JPower, Mitsui and IHI Corporation. The project has received financial support from the Australian, Queensland and Japanese governments. Within the project, IHI Corporation of Japan has responsibility for the oxyfuel retrofit work to the boiler. During the design process, several risk areas were identified that could potentially affect commercialisation prospects, safety, and reliability of operation (Yamada and others, 2009). These were:

- possible ignition of fly ash at the high temperature and high O₂ concentration on the duct wall;
- unbalanced O₂ concentration at the burner windbox inlet, resulting in a different or uncontrollable flame temperature in the four burners;
- change of boiler heat balance;
- a back stream of RFG;
- reliable performance of the flame detector.

However, tests have since confirmed that the possibility of operational problems resulting from these issues appears low. As the plant will be operating without either SCR or FGD, it will be possible to assess the effects of higher NO_x and SO_x within the CO₂ compression plant and primary recycle lines. Effects on the coal mill will also be of relevance for larger-scale operations (Wall and Stanger, 2010).

Once fully operational, the plant will enter a two- to four-year demonstration phase (Santos, 2011). This will be accompanied by an RD&D programme aimed at facilitating the commercialisation of the technology. As part of this, various longer term design issues have been flagged up as warranting attention. These include:

- the need or otherwise to dry the primary gas to the mills;
- choice of materials in the RFG circuit to minimise the impact of dew point corrosion;
- burner design – in the context of relative flows/velocity between primary gas through the burner and secondary gas around the burner registers;
- integration of heat recovery with traditional feedwater heating systems;
- process control, especially regarding run-up and master fuel trips.

As Callide will be the first integrated oxyfuel demonstration plant with electrical generation, it will be used to assess the ability of such a plant to operate with real time load following in an open market (Davidson, 2010). A two-year test programme will address issues of reliability, turndown, process and

recycle optimisation, environmental emission performance testing, and materials and corrosion testing and monitoring. Areas planned to be addressed during the demonstration programme include (Uchida, 2011):

- boiler inlet and outlet O₂ concentration change testing/controllability;
- minimum load attainable;
- load swing;
- MFT test/fan trip test;
- reliability run (continuous running);
- coal change test;
- minimisation of air-oxyfuel mode change time;
- flow meter accuracy;
- flame detector performance.

By mid-2011, the oxyfuel additions and modifications to the coal-fired plant were nearing completion. This included the installation of two new wall-fired burners, new ducting for flue gas recirculation, a recirculated flue gas moisture removal system, and new heat exchangers for cooling the flue gas. Two cryogenic air separation units (combined oxygen production capacity of 660 t/d) were also under construction. In addition, a four-stage CO₂ compressor and CO₂ concentration plant was being installed. The first stage of commissioning of the project began in March 2011. This began with the oxygen plant.

Once oxygen is available, boiler operations will begin. Initially, this will start in air-fired mode and will subsequently switch slowly to oxy-firing, with flue gas being recycled and mixed with oxygen. Once safe boiler operation has been achieved, the system will be tuned to optimise the flue gas recirculation rate and CO₂ recirculation quality. Around 15% of the recycled flue gas will be taken off for compression and treatment in the CO₂ plant. It is expected that this part of the process will be commissioned during 2012. The schedule (as of early 2012) for the operating and commissioning status of the plant is shown in Table 18. In April 2012, it was reported that commissioning was under way and that for the first time, the plant was being operated in oxyfuel mode. Full operation of the oxyfuel boiler and CO₂ capture systems is expected later in the year.

Table 18 Commissioning and operating schedule for Callide oxyfuel plant (Spero and others, 2011; Gotoua and others, 2011)	
Plant section	Timescale
Boiler	<ul style="list-style-type: none"> – air fired coal commissioning – April-May 2011 – air fired hot commissioning – April-October 2011 (completed by July 2011) – oxyfiring hot commissioning – December 2011-April 2012
Oxygen plant	<ul style="list-style-type: none"> – ASU 1 commissioning – August 20 – December 2011 – ASU 2 commissioning – September – December 2011
CO ₂ plant	<ul style="list-style-type: none"> – ASU 2 commissioning – September – December 2011 – CPU cold commissioning – November 2011–January 2012 – CPU hot commissioning – February 2012
Demonstration	March 2012 onwards
CO ₂ storage site selection	Evaluation and trial drilling to be undertaken

Daqing CCS Demonstration Project, Heilongjiang, China

China Datang Corporation and Alstom have signed a MoU to form a long-term strategic partnership to jointly develop CCS demonstration projects in China. Under the terms of the MoU, the two companies will develop two CCS demonstration projects located in China's two biggest oilfields,

Daqing and Dongying. One will be at the lignite-fired Daqing cogeneration plant in Heilongjiang Province where a 350 MWe (TRL-9) supercritical PCC boiler will be equipped with Alstom's oxy-firing technology. In November 2011, Datang and Alstom signed a feasibility study agreement for the demonstration project. This is scheduled for operation in 2015 and, when fully operational, is expected to be capable of capturing $\sim 1 \text{ MtCO}_2/\text{y}$ – the first such large-scale CCS demonstration project in China and Asia (Alstom, 2011). Some captured CO_2 will be used for EOR purposes in the adjacent Daqing oilfield and the remainder stored geologically in the Songliao basin. As well as the environmental benefits, the project also has potential for significantly lower costs than many overseas CCS projects. This will be achieved through the use of localised design and procurement.

In Yingcheng, Hubei Province, another Chinese oxyfuel project is being developed. This will focus on a 35 MWth pilot plant and is being supported as part of the MOST 863 programme. The project is being led by Huazhong University and others. Captured CO_2 (100 kt/y) is expected to be stored in existing salt mines. Start-up is scheduled for 2014.

A further Chinese project is being developed at Taiyuan in Shanxi Province (the *Shanxi International Energy Oxyfuel Electrical Generation Demonstration Project*). Air Products, Babcock & Wilcox, and WVU are working with Shanxi International Energy Group Co Ltd (SIEG). As part of this arrangement, a feasibility study and reference plant design on Air Products's proprietary oxyfuel CO_2 purification technology is being undertaken. The focus for this will be a new 350 MW supercritical coal-fired cogeneration plant belonging to SIEG. This uses $\sim 7 \text{ kt/d}$ of coal. The project aims to capture more than $2 \text{ MtCO}_2/\text{y}$, although the type of storage or utilisation has yet to be decided. As part of the project's development, the US Department of Energy and China National Energy Administration have included this project in the US-China Fossil Energy Protocol, aimed at promoting scientific and technological co-operation between the countries. In 2010, SIEG and West Virginia University conducted a pre-feasibility and related carbon management study. In the same year, MoUs were signed between Shanxi Province and West Virginia University, SIEG and APD (on oxyfuel purification), and SIEG and WVU (on CO_2 utilisation and storage). In 2011, Shanxi Province Development and Reform Commission organised the project pre-feasibility study review. In August 2011, the Reform Commission granted 4 million Yuan towards the project and arrangements for the project appear to be on track.

Young-dong oxyfuel project, South Korea

The Korean government aims to achieve commercial deployment of CCS plants and global technology competitiveness by 2020. Two LSIPs are currently under development, one of which is the *CCS 2 Oxyfuel Combustion Project* that is expected to capture $1.2 \text{ MtCO}_2/\text{y}$ for storage in a deep saline formation by 2019 (GCSSI, 2011). This will be a 100 MW repowering project located on the 125 MWe (TRL-8) anthracite-fired Unit 1 of the Young-dong power plant. The existing boiler is a BHK single drum radiant heat type, operating with main steam conditions of $541^\circ\text{C}/12.85 \text{ MPa}$. It is due to be decommissioned in 2013.

The overarching goal of the project will be the development of a competitive oxyfuel firing technology suitable for full-scale plant application, plus demonstration of a 100 MWe class oxyfuel PCC-based power plant. A phased approach is being adopted towards the development and demonstration of the technology. Phase I of the development plant (2007-10) covered fundamentals, technologies and conceptual design. KEPRI and KOSEP were involved in research and conceptual design development that covered designs for an oxy-PC combustor, optimisation and integration of an oxyfuel boiler, and examination of systems for SO_x and particulate control. Phase I involved mainly KEPRI, KOSEP, DIGC, DHIC, and KITECH; Phase II – DHIC; and Phase III – KIMM, KC-Cottrell, Yonsei University and KAIST (Kim and others, 2011).

Phase II (2010-12) is focused on the design of the oxy-fuel combustion system. This includes basic and detailed design of the proposed demonstration plant, to be fired on subbituminous or bituminous coal (Kim, 2009). Other areas being addressed include pilot plant operation, plus preparation for

construction, and development of key technologies. KOSEP will concentrate on boiler and combustion issues and burner development. Environmental control, such as flue gas cleaning, will be addressed by KIMM and KOSEP. These efforts will culminate in the production of a detailed design for the 100 MW demonstration plant. Phase III (2012--15) will focus on detailed design and repowering issues, followed by the plant's construction. The project will be co-ordinated by KEPCO. KIGAM will address issues associated with CO₂ storage. It is anticipated that commercialisation at a 500 MWe scale will take place between 2017 and 2020, to be followed by development of an advanced PCC-based oxyfuel plant post-2020.

There are a number of major technological objectives associated with the programme. These include performance optimisation and the control and management of incondensable gases (Ar, N₂, O₂).

Combustion issues include minimising NO_x formation, and the effect of excess oxygen. Others areas to be examined include purification, compression and utilisation of captured CO₂. At present, there is no storage capacity available at Young-dong (Kim, 2009). Development of potential storage options is currently lagging behind the oxyfuel development; at commercial scale, there is the possibility that eventually, captured CO₂ could be stored off-shore (Kim and others, 2011). Studies indicate that a recently discovered undersea sedimentary layer (beneath the East Sea) should be capable of holding up to 5.1 GtCO₂. Data collected by the Korea National Oil Corporation indicates a layer of porous and permeable sandstone covered with water resistant clay in the Ulleung Basin. The sedimentary layer has a thickness of between 800 and 3000 metres.

Europe

Germany – Vattenfall 30 MW Schwarze Pumpe pilot plant

This ongoing project (TRL-7) encompasses burner operation evaluation, testing of major boiler impacts, emissions assessment, and CO₂ compression (*see* Figure 17). The plant configuration also has the potential for the evaluation of other operations such as limestone addition for sulphur capture and ammonia addition for NO_x reduction. It has been designed to have flexibility in terms of construction and the ability to change components such as burners. Since starting CO₂ capture, the plant has been modified on a number of occasions; there have been two rebuilding periods to enlarge the project and changes have been made to three different burners for testing purposes.

Operating experience has confirmed that the plant can be switched easily from air firing conditions to oxyfuel firing in only 20 minutes. Good flame stability has been obtained at oxygen concentrations in



Figure 17 Vattenfall's oxyfuel Schwarze Pumpe pilot plant in Germany (photograph courtesy of Vattenfall)

excess of 21 wt% although different burner swirls are necessary for air and oxyfuel operation. Burners have been shown to operate in premixed mode in a stable and reliable way with an oxygen concentration of 28 vol% (Davison, 2010). It was determined that in oxyfuel mode, emission limits could be achieved easily. Primary measures for NO_x control were found to be unnecessary as emissions were typically <700 mg/m³ (dry). Burnout was good with low unburnt carbon in the fly ash and slag. CO₂ concentrations in the flue gas

downstream of the boiler were >85 vol% (dry). By late 2009, the plant had operated on lignite for over 3000 hours, with oxyfuel conditions being applied for slightly more than half of this time. Vattenfall announced that it was achieving nearly 100% CO₂ capture.

In May 2011, Air Products' proprietary CO₂ capture technology (encompassing capture, purification and compression) went on line at the plant. Air Products' sour compression technology uses a staged compression process to optimise operating conditions and achieve an adequate residence time to allow for removal of impurities during the compression process. This reduces costs and minimises the concentration of acidic components in the CO₂ prior to handling. In the same month, the first deliveries of CO₂ from the plant were taken by truck to the Ketzin storage test site. Since commissioning in September 2008, the plant has now operated for >12,000 hours. During this time, more than 8900 tCO₂ has been captured and liquefied. This was close to food grade quality and suitable for pipeline transport and storage (Burchhardt and others, 2011).

As part of the programme, sulphur-rich recirculation gas has been tested (downstream of the ESP, but upstream of the FGD). Operating experience was gained in pre-mixed operation mode (oxygen fed into the recirculation stream) as well as with oxygen fed into individual burner ports. Different ignition burner concepts have been tested and various burner configurations assessed. A combined jet/swirl burner and two pure swirl burners have been tested. Since beginning operations, the combustion behaviour under oxyfuel conditions has been significantly improved. The intention has been to restrict the level of excess oxygen at the boiler exit to less than 5% in order to maintain a high level in the oxygen-enriched combustion gas. A low O₂ surplus in the waste gas reduces the oxygen demand for combustion, whereas a high level results in a low recirculation rate. Both arrangements have direct impact on the efficiency of the oxyfuel process. Alongside assessment of combustion behaviour and heat transfer in the oxyfuel boiler, the flue gas cleaning process (using an ESP, FGD and flue gas condenser to provide the required flue gas composition for the CO₂ process) has been examined. Studies have confirmed the suitability of the conventional power plant components and that adequate removal rates of particulates and SO_x can be achieved (Burchhardt, 2011).

CO₂ processing (compression and purification) forms an important component of project. Although neither are new concepts, they are relatively new for oxyfuel applications. Thus, a compression/purification system designed by Linde has (since 2008) been under test at the plant. The processing unit is located downstream from the flue gas cleaning processes. A series of tests have been carried out with particular focus on technical and operation issues (Yana and others, 2011).

Overall, for the first time, plant operations have confirmed a number of important aspects of oxyfuel firing. These have included combustion behaviour of lignite under oxyfuel conditions, the interaction of components originating from the chemical industry with power plant technology (air separation, boiler, flue gas cleaning, and CO₂ plant), achieving the necessary CO₂ purity for transport and storage and compliance with emission requirements. As part of the latter, the influence of the burner, overfire-air/oxidant and air in-leakage was assessed. Various options (such as use of combined deSO_x and deNO_x processes during flue gas cleaning) are being considered.

Despite the significant advances made during the past three years, Vattenfall sees potential for increased efficiency of the oxyfuel process and a number of areas have been identified for further research and development (Burchhardt and others, 2011). These include:

- optimisation of individual plant components (such as ASU and CO₂ plant);
- improved availability of materials for use of hot sulphur-rich recirculation for large units;
- integration of a pressurised fluidised bed dryer (PFBD) for lignite with vapour compression;
- application of membrane technology for oxygen production;
- further investigation of the compression process (vibration behaviour when using CO₂-rich flue gas);
- operating behaviour of activated carbon filters;
- drying processes based on molecular sieves;

- vent gas composition and how to use it;
- aspects influencing CO₂ quality.

A planned series of combustion tests is still to be completed. These will address a number of issues such as the impact of varying coal type and quality (moisture and sulphur contents, and particle size).

Cofiring tests, using combinations of biomass and bituminous coal, are also planned. This will be accompanied by further assessment of different burner designs, as well as tests addressing the suitability of materials for plants operating at 700°C under oxyfuel conditions. There will also be an examination of how to further reduce NO_x levels when in oxyfuel mode.

Overall, the Schwarze Pumpe plant is providing useful experience on the capture and processing of CO₂. It is demonstrating the full process from coal input and oxygen production, through to CO₂ separation. Full load operations have been confirmed in both in air and oxyfuel modes. It is anticipated that data being produced by the ongoing development programme will be sufficient to take the technology on to the larger demonstration stage. The overarching goal is to provide operating information and experience to enable scaling-up of the technology to a 400–600 MW demonstration power plant.

The next stage in the development of the technology was to be a scaled-up 250 MW lignite-fired demonstration project, planned for the 1 GW Jämschwalde power plant in Germany. Between 1.5 and 2 MtCO₂/y was to be captured and stored in depleted reservoirs in the Altmark gas field. However, in September 2011, it was announced that Vattenfall had put the project on hold.

Spain – CIUDEN oxyfuel programme

The Fundación Ciudad de la Energía (CIUDEN) is undertaking a CO₂ capture programme based around a large-scale experimental plant at El Bierzo, close to the Compostilla power plant. This is intended to allow RD&D using a wide range of coals and incorporates two different oxyfiring systems, namely pulverised coal and circulating fluidised bed technologies. The intention is that the facility will be operable under a wide range of conditions and be capable of modification in order to address other areas that may arise as oxyfuel technology develops further.

CIUDEN is undertaking a *Technology Development Plant (TDP)* RD&D programme. This has two overarching goals. The first is the validation of the full process chain, from fuel preparation to CO₂ purification and production of a stream ready for transport and storage; this is under way. The second is to produce data for scaling up the oxyfuel process for both PCC and CFB-based options. As part of this, investigations are focusing on coal preparation and feeding, the development and evaluation of flue gas recirculating/mixing and heating devices, flue gas cleaning issues, and CO₂ purification and compression. A series of different oxygen/RFG compositions will be tested, allowing the impact of different oxygen concentrations and mixtures to be assessed. Research topics will include effects of variable oxygen concentration on corrosion, avoiding the possibility of early combustion, and control of moisture content in the solids transport stream so as to avoid condensation on cold system surfaces. Systems will be tested under different simulated power plant operating conditions, such as start-up, shut-down and load following. In addition, tools for boiler design, dynamic simulation, and performance prediction are being developed. Other areas of activity will include the development of advanced materials suitable for application in oxy-firing systems (Cortes, 2011).

In order to minimise the economic and technical risks associated with the oxyfuel process, the CIUDEN project is being taken forward in two distinct phases. Phase I covers technological development (2009–12), and Phase II, technology demonstration (2013–post-2015). Phase I includes the construction of three pilot scale TDPs for CO₂ capture, transport and storage. Operation of these will provide experience and technical support for Phase II. The CO₂ capture and transport TDPs are under construction and the storage TDP (at Hontomin) is currently undergoing detailed geological characterisation. A comprehensive RD&D programme is planned for Phase I (Table 19).

Table 19 CIUDEN planned RD&D oxyfuel programme (CIUDEN, 2010)

Area	Scope of activities
Combustion process and boilers	<ul style="list-style-type: none"> – combustion arrangement and fuel preparation – heat transfer and modelling – heat transfer and modelling – heat transfer and modelling combustion, ignition and flame stability + CFD models – heat transfer and modelling mineral matter: ash, slagging and fouling – heat transfer and modelling formation and reduction of pollutants: NO_x, SO_x and others – heat transfer and modelling formation and reduction of pollutants: NO_x, SO_x and others – heat transfer and modelling advanced process simulation – heat transfer and modelling tools development for scale-up
CO ₂ purification and compression	<ul style="list-style-type: none"> – pollutants separation technologies evaluation – inerts and impurities removal from product gas – flue gas treatment and CO₂ compression/purification integration
DeNO _x unit	<ul style="list-style-type: none"> – catalysts tests – new reactants development and tests for SCR – combustion/SCR/SNCR optimisation – CFD Modelling
DeSO _x unit	<ul style="list-style-type: none"> – CFD Modelling high CO₂ concentration effects in DeSO_x – CFD Modelling components design and absorbents tests – CFD Modelling development of catalysts for Hg capture and oxidation
Materials	<ul style="list-style-type: none"> – CFD Modelling development of catalysts for Hg capture and oxidation in high gas temperature/O₂ enriched environments – CFD Modelling development of catalysts for Hg capture and oxidation influence of S and Cl on high temperature corrosion of structural steels – alternative materials tests
Operation safety and integration	<ul style="list-style-type: none"> – Hazard and Operability Studies (HAZOPs) – start-up and shut-down routines – interactions between units. Interactions analysis via comprehensive models
Units and components	<ul style="list-style-type: none"> – thermo-economic and environmental simulations of units and overall plant – advanced control for units and overall plant integration – transient periods simulation in systems and components – transient periods simulation in systems and components

The El Bierzo plant incorporates both 20 MWth pulverised coal and 30 MWth circulating fluidised bed boiler TDPs (both TRL-7), both operable in air or oxyfuel modes. The former incorporates two arch burners and can accommodate up to four front burners for the study of flame interactions within the unit. It consumes 3.35 t/h of coal and 6.6 t/h of oxygen. The fuel preparation system can process a range of fuel types that include anthracite, petcoke and bituminous coals. The plant also has flue gas cleaning and compression systems. In May 2011, as part of the PCC development programme, stable and simultaneous ignition (using natural gas) of four of the unit's burners was achieved (Diego and others, 2011). Phase II (2013-15) will confirm the operability of the system and focus on scaling up the oxyfuel technology, plus address CO₂ transport and storage infrastructure. A major aim will be to confirm the flexibility and competitiveness of the system for retrofitting to existing power plants at a commercial scale. Specific goals include technological development and innovation in the areas of:

- CO₂ capture (capture rate expected to be >90%) – design and operation of the boiler, CO₂ flow processing, oxygen-related safety issues, integration of units;
- CO₂ transport by pipelines - impact of impurities on pipeline materials, optimisation of transport conditions;
- CO₂ storage – development and optimisation of injection strategies, establishment of methodologies to monitor the injected CO₂, and investigation and understanding of the long-term processes that control CO₂ geological storage. CO₂ will be stored in a nearby saline aquifer. It is estimated that 5 Mt will be stored during the first five years of plant operation.

Plant operability will be investigated using a wide range of domestic and imported coals, plus other fuels such as petcoke and biomass. As part of this, investigations will include biomass co-combustion, the design of possible supercritical process sections, and the evaluation of novel technologies for air separation (mixed conductive membranes). Chemical looping oxy-combustion will also be examined; this will include pilot-scale testing of direct chemical looping applied to coal, ash/O₂ carrier separation, and testing of new O₂ carriers. Another area earmarked for future RD&D activities is examination of high oxygen oxy-combustion systems, with a view to developing second generation oxyfuel fired power plants (Cortes, 2011).

As part of the PISCO2 project, CIUDEN is developing a system for monitoring the security of CO₂ geological storage and identifying potential leakage. Soils from above the proposed CO₂ storage site at Hontomin are being assessed; continuous monitoring systems will measure water content, pH levels and CO₂ fluxes, and also assess potential microbiological, botanical and geochemical changes.

The oxy-CFB development programme

The oxy-CFB testing programme aims to develop and demonstrate a power plant concept based on a 30 MWth (TRL-7) Foster Wheeler *Flexi-Burn* CFB unit (operable under conventional air or in oxy-combustion mode) combined with CCS. This scale of unit is considered to be sufficient to allow the scaling-up of plant data to commercial sized units, whilst minimising investment cost and operating expenses. The boiler consumes around 5.5 t/h of coal and 8.78 t/h of oxygen. Around 46 t/h of steam at 3 MPa/250°C is produced (Cortes, 2011). The oxidant for the CFB unit is divided into independent streams (primary and secondary), each with a specific function. Primary oxidant enters into the bed via the fluidisation grid, providing a low oxygen atmosphere. The remainder of the primary oxidant is supplied through upper nozzles. Secondary oxidant is supplied at different levels to provide the appropriate conditions to complete the combustion process and control the emissions. CIUDEN suggests that CO₂ concentrations in the flue gas could reach ~60%, as opposed to 15% with conventional air combustion.

The preliminary test programme will examine the effects of a number of parameters that include bed temperature, excess O₂ concentration, oxidant concentration, fluidisation velocity, flue gas recycle, sorbent addition, bed inventory, SO₂ abatement, and corrosion/fouling/agglomeration issues. Thus, major programme goals include:

- demonstration of oxy-combustion in a 30 MWth CFB;
- testing of a range of fuels under different operating conditions;
- generation of data for model validation and technology scale-up;
- determination of optimum operating parameters to allow sizing of new full scale oxy-fired units;
- obtaining combustion behaviour data for different coals under conventional and oxy-combustion conditions;
- comparison of performance of air and oxy-combustion modes;
- provision of flue gas stream for testing and demonstration of post-combustion carbon capture equipment (when operating in air-fired mode);
- provision of a CO₂-rich gas stream for equipment testing (operating in oxy-combustion mode);
- developing fully equipment for CO₂ purification and compression;
- obtaining data to evaluate impact that oxy-combustion conditions may have on combustion, emissions and on radiant and convective boiler surfaces.

Table 20 Major aims of the OXYCFB300 Compostilla Project (Lupion, 2011)	
Area	Scope of activities
CO ₂ capture	<ul style="list-style-type: none"> – basic engineering of capture OXYCFB 330 MWe unit – design, construction and operation of a capture TDC at pilot scale (30 MWth) – validation tests at Capture TDC in order to scale-up the technology – develop models for optimising the final design for oxy-combustion – develop models for optimising the final design for oxy-combustion capture studies economic and risk assessment
CO ₂ transport	<ul style="list-style-type: none"> – preliminary studies – singular studies: conceptual and basic design, risk, monitoring and safety studies – design, construction and operation of a Transport TDC at pilot scale – transport economic and risk assessment studies
CO ₂ storage	<ul style="list-style-type: none"> – site assessment – preliminary characterisation of the subsurface structures – extensive subsurface characterisation – design, construction and operation of a Storage TDC at pilot scale – storage economic and risk assessment studies

In September 2011, the CFB unit was fired for the first time using coal. Operation was successful with no major unexpected operational characteristics observed. Initial operations and commissioning activities continued throughout the latter part of the year. As part of this, the unit was operated (in conventional air-combustion mode) using anthracite from the El Bierzo region of Spain. Data generated during this test were in line with expectations; the boiler showed stable operation at full load and the auxiliary equipment ran successfully under varying operational conditions.

A full period of CFB testing is planned for 2012-13. This will encompass a wide variety of fuels and blends that include local anthracite, petcoke, bituminous coal, lignite, and biomass. Testing will generate data on the combustion behaviour of the different fuels under conventional and oxy-combustion conditions. This will be used for model validation and to ease scale-up to commercial sized operations (Hacka and others, 2011). Areas to be examined will include CO₂ purification and compression, and the impact of oxy-combustion operation on combustion, emissions, and corrosion of boiler heating surfaces. The CO₂ purification and compression unit will also be started up during this period. This will complete the integration of the CO₂ capture system, making it ready for transport and storage.

Once the CFB-based technology has been developed fully and tested on the 30 MW TDP, this component of the programme will be taken forward via the scaled up *OXYCFB300 Compostilla Project*. The aim is the validation of oxy-CFB combustion with CCS at an industrial level (Alvarez and others, 2011). The Compostilla project is being co-financed by the EU's Energy Programme for Recovery and will be based on a 300 MWe (323 MWe gross) (TRL-9) oxyfuel CFB plant operating under supercritical conditions. Around 1.1 MtCO₂/y will be captured and stored in a deep saline formation. The project is being led by a consortium comprising ENDESA (project coordinator and owner of the Compostilla power plant), CIUDEN and Foster Wheeler. The latter is the technology provider for the CFB units in the capture TDP and demonstration plant. Major aims of the project are summarised in Table 20.

However, during January 2012, it was reported widely in the European and US media that the proposed OXYCFB 300 demonstration project had been unofficially curtailed owing to a lack of committed public and private money. ENDESA, which was to build the plant based on CIUDEN's technology, has announced that it will not make any formal decision on the project until later in 2012.

Capture Power Ltd CCS project, Drax, UK

This project is being considered for the Drax power station site in North Yorkshire. The proposal is for an oxy-fired CCS demonstration (the White Rose Carbon Capture and Storage Project) based on a new coal-fired 426 MW (TRL-9) supercritical PCC unit. Alstom would supply the oxyfuel combustion system, and National Grid provide the CO₂ transportation element of the chain. Capture efficiency would be ~90% and it is anticipated that around 2 Mt/y of CO₂ would be captured and piped offshore (via a common user pipeline infrastructure) for storage beneath the North Sea. At the moment, deep saline formations are being examined although consideration is also being given to using the CO₂ for EOR purposes. This project is being developed as part of the Humber CCS Cluster concept. To date, preliminary and feasibility studies have been carried out and a project start-up date of 2016 has been suggested.

In January 2012, it was announced that BOC had joined the project. BOC was selected following a competitive process and will provide its air separation technology as well as plant engineering and integration capabilities from its parent company (The Linde Group). The entire project is being taken forward by a newly created company, Capture Power Ltd. In 2011, Alstom UK, Drax Power and National Grid applied to the EU NER300 funding competition for CCS and renewable projects. Funding is being sought from the scheme but will also be dependent on market mechanisms to incentivise low-carbon technologies. The consortium plans to apply for consent from the Infrastructure Planning Commission by early 2013. Reportedly, construction of the plant would take about three years.

ENEL CCS2 oxyfuel demonstration, Italy

The goal of the CCS2 project is the construction and operation of a 35–70 MWe (probably ~50 MWe) near-zero emission coal-fired power plant based on a pressurised oxy-combustion technology developed and proved previously at pilot scale. Project partners comprise ENEL, ENEA and ITEA.

The main objective is the development and demonstration (on an ‘industrial scale’) of a patented pressurised coal combustion process that incorporates CCS with a lower energy penalty than competing technologies. Work has been proceeding via a three-phase development programme. During Phase I, at its Livorno experimental plant, ENEL developed atmospheric pressure oxyfuel combustion technology. As part of this, oxy-coal combustion tests were undertaken successfully using different flue gas recirculation ratios. Development work was also carried out at the ITEA 5 MWth Isotherm experimental plant in Gioia del Colle to develop a pressurised form of the technology.

During Phase II of the project, the preliminary design for a full scale combustor demonstration was produced. This was to be taken forward in Phase III with the development and operation of a 48 MWth oxyfuel combustor fed with coal slurry. During 2011, reportedly, FEED and costing studies for a larger scale demonstration plant were under way. However, the status of the project remains unclear and it appears that it may not now proceed (Santos, 2011).

North America**FutureGen 2.0, Illinois, USA**

In August 2010, the US DOE announced a refocusing of the existing FutureGen programme to create FutureGen 2.0, with the aim of building one of the world’s first coal-fired near-zero emission power plants incorporating CCS. The project aims to retrofit oxyfuel technology to an existing power plant coupled with CO₂ capture and transport by pipeline to a suitable storage facility.

The focus of the project is a mothballed 200 MWe (TRL-8) oil-fired unit at the Meredosia power plant in Illinois (see Figure 18). This will be repowered with oxyfuel technology and will capture ~98% of the plant’s CO₂ emissions (at least 1 Mt/y). Other plant emissions (such as NO_x, SO_x, PM, and Hg) will be reduced to near-zero levels. The project is being taken forward by *The FutureGen Industrial Alliance* by means of a partnership with the US DOE. The alliance is a non-profit corporation



Figure 18 The Meredosia power plant in the USA, the future location of the FutureGen 2.0 oxyfuel project
(photograph courtesy of Ameren)

representing a coalition of coal producers, coal users and coal equipment suppliers. Full members include Alpha Natural Resources, Anglo American, CONSOL Energy, Louisville Gas and Electric Co, Kentucky Utilities Co, Peabody Energy, Rio Tinto Energy America, and Xstrata plc. China Group is also a member. Main technology suppliers are Babcock & Wilcox, and Air Liquide Process and Construction Inc. The existing Meredosia plant is owned by Ameren Energy Resources; Ameren's partners in the project are Babcock & Wilcox, URS and Air Liquide.

The schedule and timescale of the project has been adjusted several times although the latest information suggests that pre-FEED (Phase I) activities will be completed by June 2012, FEED (Phase II) will take place between July 2012 and December 2013, with EPC and start-up (Phase III) between January 2014 and June 2017. The test period (Phase IV) will be between July 2017 and March 2020 (McDonald and others, 2012a). Captured CO₂ will be injected and stored more than half a mile underground in the Mount Simon sandstone formation. Morgan County has been identified as the preferred storage site. The Alliance will also be responsible for the pipeline and storage facility part of the project.

The overarching goal of FutureGen 2.0 is to test technologies that will help reduce CO₂ emissions from coal-fired power generation in the USA by implementing innovative technology, allowing the country to remain competitive in a carbon-constrained economy and become a world leader in CCS. Specific objectives include:

- proving the technology on the first-of-its-kind commercial-scale, oxy-coal power plant;
- exhibiting the full integration of an ASU and an innovative CO₂ compression and purification unit into a full-scale utility application for electric power generation;
- repowering an existing 200 MW plant with oxy-combustion technology;
- validating technical and economic feasibility of the oxy-combustion technology for utility power plant applications;
- establishing a cost and schedule baseline for the technology;
- to be a Near Zero Emissions Plant (NZEP) and to treat 100% of the flue gas, removing >90% of the CO₂ (capture of at least 1 MtCO₂/y);
- confirming equipment (primarily the boiler) designs in terms of reliability (component design, materials of construction), maintainability (erosion, corrosion, outage cycles), basic process and heat transfer data, process designs (safety, functionality, operability), and integrated operation of ASU, boiler and other major components (start-up, shut-down, load swing, capacity factor, system dynamics).

The project is scheduled to proceed in four phases (*see* Table 21). The intention is that Phase IV will be followed by large-scale commercialisation of the technology (post-2018) (McDonald, 2011).

Phase I has now been completed. This included the initial engineering, design and economic analysis for repowering the unit. The partners are now validating the project's scope, cost, schedule and

Table 21 Proposed timescale for FutureGen 2.0 development

Phase	Timescale	Activities
1	Oct 2010–Oct 2011	Pre-FEED
2	Oct 2011–Oct 2012	FEED
3	Nov 2012–April 2016	Procure, construct and start-up
4	May 2016–Dec 2018	Test period

commercial viability. If the outcome of this phase is favourable and the project is judged to be technically and commercially sound, the US DOE will authorise the second phase that will cover detailed engineering design, schedule and cost analysis, and environmental studies to support the National Environmental Policy Act process and effluent permitting. Successful completion of Phases I and II studies and enactment of the supporting legislation will be necessary before Phase III is authorised. This will include the EPC activities needed to repower Unit 4 of the plant. It is anticipated that the converted

Meredosia plant will be capable of operating on different types of coal and under a variety of operating conditions. The data generated will be used to scale up and expand the market for oxy-combustion technology.

Before commencing full-scale operations, the proposed CO₂ storage site will be the subject of an extensive environment review conducted by US DOE in compliance with the National Environmental Policy Act. The site will be fully-permitted by the Illinois Environmental Protection Agency to assure its safety. Key goals of the pipeline and CO₂ storage reservoir project are to:

- facilitate validation of the technical feasibility and economic viability of near-zero emission energy from coal;
- verify effectiveness, safety, and permanence of CO₂ storage in saline formations;
- establish standardised technologies and protocols for CO₂ monitoring, verification, and accounting;
- gain domestic and global acceptance of the FutureGen 2.0 concept and facilitate broad deployment of both new and repowered oxy-combustion plants coupled with CCS.

At the end of 2011, project status was as follows:

- US DOE co-operative and teaming agreements signed in 2010;
- project team mobilised;
- Phase I proceeded on schedule;
- Worley Parsons selected as B&W's architect/engineer (A/E) in February 2011;
- US DOE and Management Phase I reviews in progress. Project definition/pre-FEED completed in September 2011.

Pre-FEED accomplishments of Ameren and its partners at the end of 2011 are shown in Table 22. FEED studies and National Environmental Policy Act permitting were scheduled for completion by October 2012, to be followed by detailed EPC and start-up in April 2016 (Moorman, 2011).

In late 2011, it was announced that Ameren planned to close the Meredosia plant by the end of the year, citing stricter air clean air rules finalised previously by the EPA. However, the company stated that the closure would not affect the FutureGen project. In December 2011, Ameren was reportedly in discussions to sell part of the plant to the FutureGen Alliance, enabling the project to proceed as planned. Around the same time it was reported that geological testing was under way examining the Mount Simon formation. As part of this, characterisation wells had been drilled into the porous sandstone and other layers of rock making up the site. Drilling has since been completed – preliminary data indicate that the local Illinois geology is suitable for CO₂ storage. The drill rig is being removed from the characterisation well site and a smaller service rig installed over the well head in order to conduct hydrologic testing. Once this has been completed, the well will be configured as a monitoring well that will be used in future phases of the project.

Table 22 FutureGen 2.0 project status – Ameren and partners pre-FEED accomplishments (end of 2011) (Moorman, 2011)		
Ameren	Babcock & Wilcox	Air Liquide
URS selected as owner's architect/engineer	Boiler/GQCS design and performance determined	ASU and CPU design, site layout plans completed
Integrated project schedule, DOR, work breakdown structure, project cost estimate completed	Site layout plans completed	Quotes for 70% of major equipment obtained
Existing plant assessment undertaken	Quotes for 85% of major equipment obtained	Specifications and bid packages for BOP determined
Project levelised cost of electricity model developed	Specifications and bid packages for BOP completed	PFDs, control architecture, interface list completed
Federal and State government affairs, Illinois EPA efforts on-going	Preliminary piping and instrumentation diagrams, process flow diagrams (PFD) completed, instrumentation and control architecture completed	High level construction plan developed
Draft Phase 1 Decision Application in progress	High level construction plan developed	

Following the completion of the initial Phase I pre-FEED work, it was discovered that project costs were higher than anticipated. As a result, it was deemed necessary for FutureGen 2.0 to be redesigned.

Cost reduction measures were identified that would bring the cost back within the initial budget. Following AER's withdrawal, the FutureGen Alliance has been working with AER, B&W and Air Liquide to assume the role of owner for both the capture and storage parts of the project. Financing for the complete facility is still to be arranged, as well as capital support for the cost share of the capture plant and redesigning the project structure (McDonald and others, 2012b). In order to support these efforts, the US DOE granted a Phase I extension to reconfigure and develop updated costs and performance for the smaller capture plant and for the Alliance to put the basic agreements in place. Work began in January 2012 and the revised Phase I report was submitted to the US DOE in April. In order to drive significant cost reduction, several key changes were made. The design coal (originally 100% Illinois coal) was switched to a 60% Illinois: 40% PRB blend (1149 t/d and 766 t/d respectively), significantly reducing sulphur and chlorine removal requirements. In addition, the unit was redesigned for 168 MW gross output (rather than the original 200 MW). There is a continuing requirement for a minimum of 90% CO₂ capture (in practice, it will be >98%); current estimates suggest that ~1.08 Mt/y CO₂ will be captured. In mid-2012, the Alliance directors approved the project to proceed to Phase II and the Phase I Topical Report was submitted to DOE for review. Following this, the US DOE will decide whether to proceed to Phase II.

6.1 Future RD&D focus and challenges – oxyfuel

Oxyfuel combustion is one of three main routes being pursued towards the economic capture and storage of CO₂ from coal-fired power plants. However, it has yet to be demonstrated at utility scale. The GCSSI considers that the integrated oxyfuel technology is at a lower level of technical readiness than competing systems such as post-combustion capture and IGCC + CCS; these are considered to be closer to commercial realisation.

Table 23 Oxyfuel combustion - areas identified for further RD&D (Dave and Duffy, 2002; VGB, 2004; GCSSI, 2009 and 2012e; Ciferno, 2010; ZEP, 2010b; Wall, 2010; Wall and others, 2011; Santos, 2011)	
Oxyfuel combustion	Flame management with recycle (PCC)
	Air/oxy mode switching
	Burner design and aerodynamics (PCC)
	Radiative heat transfer issues
	Impacts of air leakage into boiler
	CFD modelling
	O ₂ mixing
	Detailed analysis of combustion chemistry and kinetics needed to provide design data
	Ash behaviour under oxyfuel conditions
	Fate of SO ₂ and NO _x emissions
	Bed control and recycle (CFBC)
	Improved understanding of slagging and fouling mechanisms
Fuel supply	On-line coal milling with recycle
	Lignite drying
	Fuel conveyance and mode switching
	Improved understanding of use of lean fuels such as anthracite and LV coals
Oxygen supply	Reduction of energy penalty
	Reduction in capital costs of ASU
	Improved/new ASU/power plant integration
	Optimised ASU for open market
	Non-conventional O ₂ supply
Electrical generation	Plant integration and optimisation
	Materials for USC operations with oxyfuel
	Plant operation in open market
	Plant availability
	Heat transfer and radiation
	Dynamic behaviour and start-up/shut-down procedures need evaluation and development

Oxyfuel combustion/CO₂ capture power plant designs being developed and demonstrated within the next four to five years are based on individual component technologies and arrangements that have demonstrated sufficient maturity. The greatest remaining technical challenge is integrating the systems into a complete steam-electric power plant (Oettinger, 2012b). Various issues require addressing before oxyfuel can be confirmed fully as a viable option for utility-scale applications. At the moment, the technology is viewed as being semi-commercial, in that even if a unit was economically viable and could be provided by a vendor, the generator and vendor would need to share the technical risk. This is because guarantees could not at present be provided for operating characteristics associated with mature technologies such as reliability, emissions, ramp rate and so on. The situation is governed by the current technical capabilities of vendors and associated design and operational uncertainties and results largely from the lack of plant experience at semi-commercial and commercial scale. However, the development of oxy-fuel technology is fast approaching the demonstration stage and, as noted above, there are several large-scale projects receiving financial support from the European Union, the US DOE, and the Australian Government.

Table 23 Continued	
Flue gas treatment & cooling	Reduction of overall cost of electricity generated
	Impurity behaviour and control (NO _x , SO _x , Hg, H ₂ O)
	Conventional – low NO _x burner, SCR, FGD, ESP/FF
	Non-conventional - limestone injection, fly ash capture, NaOH scrubbing, high pressure scrubbing
	Flue gas cooling (direct or indirect)
	Activated carbon bed for Hg control
CO ₂ compression and inerts removal	Large-scale flue gas compression
	Reducing cost of CO ₂ purification
	CO ₂ auto-refrigeration
	Dehydration
	Inerts off gas re-processing (higher capture rate)
	Circuit optimisation (cost, energy, capture rate, product purity)
Transport & storage	Pipeline materials and infrastructure
	CO ₂ product purity
	Site characteristic and injection rates
	Regulations and long-term liability
	Public acceptance
Materials issues	Selection and evaluation of materials suitable for oxyfuel conditions
	Impact of high coal sulphur levels on construction materials
	Development of materials with enhanced corrosion resistance
	Improved understanding of corrosion processes

Studies suggest that, potentially, a significant number of existing coal-fired power stations could be converted to oxyfuel combustion with relatively little change to the plant water-steam cycle, and require only minimal modifications to the boiler island. Limited alterations to the air quality control system would be required. Clearly, major equipment additions would be needed that would include an ASU, oxyfuel-fired burners, flue gas recycle system, and CO₂ compression and handling facilities. It is generally assumed that converted power plants would be capable of operating in both air- and oxy-fuel modes (Song and others, 2010). However, although retrofitting many existing power plants is regarded as technically feasible, all process variants require further optimisation in order to reduce the cost and efficiency penalty of CCS.

The major development challenges highlighted for oxyfuel systems are summarised in Table 23. Many are common to other types of capture system being developed and focus on cost and energy requirement reduction, and demonstration of integrated operation at larger scale. Thus, some of the development activities under way are similar to those being developed for both post- and pre-combustion capture. However, with regard to oxy-combustion systems, the most compelling need (and a major focus of R&D) is for the development and application of improved, lower-cost systems capable of delivering large quantities of high-purity oxygen; in current oxyfuel schemes, this is the major cost item. However, there are also a number of other areas that are the focus of ongoing RD&D.

Recent US studies suggest that future process efficiency improvements point towards a plant with near zero-emissions of conventional pollutants, up to 98% CO₂ capture, and efficiency comparable to the

best power plants currently being built (Oettinger, 2012b). The ongoing development programmes associated with the current crop of oxyfuel pilot plants should help resolve many of the outstanding issues.

Many of the issues highlighted in Table 23 are being addressed as parts of major RD&D programmes being undertaken in Europe, Asia and North America. For instance, in the USA, oxyfuel developments for PCC boilers are being pursued by a major NETL-led programme involving technology developers and vendors that include Praxair (O₂ membranes, CO₂ purification), Air Products (CO₂ purification), Jupiter Oxygen (burners), Alstom (pilot plants), Babcock & Wilcox (cyclone pilot tests), Foster Wheeler (corrosion), Reaction Engineering International (retrofit), Southern Research Institute (retrofit), and the NETL Office of Research and Development (modelling, CO₂ purification).

One of the greatest remaining technical challenges is integrating oxy-fuel systems into a complete steam-electric power plant. The oxy-combustion/CO₂ capture power plant designs currently being developed and likely to be deployed in the immediate future have been based on individual component technologies and arrangements that have demonstrated sufficient maturity. However, such plant designs may not be optimised and as technological development continues, it is likely that evolutionary changes in oxy-combustion plant flow sheets (with CO₂ capture) will result in reduced capital and operating costs and improved plant performance (EPRI, 2012). The GCCSI considers that oxy-combustion is on track to achieve commercial scale operation by 2020, although technology developers will require significant financial support for their scale-ups from present pilot plant size (30–40 MWth). As is the case for post-combustion capture, funding for the scale-up of technologies beyond this scale remains a key issue for oxy-combustion capture R&D (GCCSI, 2012b).

6.1.1 Materials development issues

In common with other technologies that incorporate CO₂ capture, oxyfuel systems must be constructed from materials capable of withstanding the conditions imposed. These must exhibit sustained performance and withstand possible combinations of high temperatures and pressures, chemical attack, wear, and alternating oxidising and reducing conditions. The oxyfuel combustion process necessarily implies a new combustion atmosphere and since nitrogen is replaced with recirculated flue gas, higher concentrations of species such as SO₂, SO₃, CO₂, H₂O and O₂ are likely to be encountered. Potentially, this creates a more aggressive environment. Therefore, a crucial issue is to identify suitable, cost-efficient alloys and other materials suitable for sustained use in this type of environment.

In oxyfuel power plants, the flue gas comprises mainly H₂O and CO₂ although there may also be some unconsumed oxygen and fuel-specific impurities. Oxyfuel systems involve circulating a proportion of CO₂-rich flue gas back into the boiler, where it replaces nitrogen, diluting the oxygen concentration to an appropriate level. If this split occurs before any FGD system, the boiler has to operate with much higher sulphur (and possibly chloride) levels that may increase corrosion-related issues. If recirculation occurs post-FGD, there will be a large efficiency loss, although sulphur levels will be relatively low. During operation, metallic components of oxyfuel systems must be capable of resisting surface temperatures of up to ~650°C in coal burning power plants, although future supercritical/ultra-supercritical facilities are expected to operate at up to 700°C or more. Compared to conventional combustion-based processes, less data is currently available for oxyfuel systems and less is known about the oxidation resistance of different steels/alloys under these conditions. Globally, for some years, a considerable body of RD&D work has been under way, focused on the development and selection of more advanced alloys suitable for operation under advanced steam conditions and/or more aggressive environments.

From a materials degradation and corrosion standpoint, there can be a wide range of environments amongst the different carbon-capture processes. Where an atmosphere is characterised by high CO₂

and moisture levels (as in oxyfuel systems) it tends to be acidic, potentially resulting in high corrosion rates for unprotected carbon steel. Corrosive conditions are expected to increase throughout the boiler as well as in localised furnace wall zones (Robertson and others, 2011). Corrosion-related processes can be general in nature or more localised and a number of different mechanisms can be involved such as erosion-corrosion, stress-corrosion, low temperature hydrogen damage, microbially-influenced corrosion, high temperature hydrogenation, sulphidation, and liquid metal embrittlement (Billingham and others, 2011). Even in small quantities, the presence of components such as chlorides, SO_x, O₂ and H₂S in a process stream can have significant effects on the severity of the environment. For instance, although the SO₂ content of inlet gas may be low, it is soluble in water and there is a risk of dew-point corrosion from small volumes of acid mist or condensation in inlet ducting and pipework. Furthermore, reactions involving NO_x and SO_x can be complex and vary depending on the prevailing condition of the power plant (steady-state, start-up, shut-down, etc).

Historically, a number of programmes have focused on the development of alloys suitable for the extreme conditions experienced under, for instance, ultra-supercritical steam conditions and a number of advanced alloys have been developed successfully from these programmes. However, more recently, the growing interest in oxyfuel combustion has increased emphasis on the behaviour of materials under these new conditions. Studies focused on materials development and capabilities are ongoing in several parts of the world. For instance, in Germany, for some years, several major materials development programmes have been under way. As part of this, work is examining the corrosion behaviour of power plant steels and nickel-based alloys with different chromium contents in contact with combustion gases comprising H₂O, CO₂ and O₂. Data suggests that, unexpectedly, under oxyfuel conditions, some power plant steels and alloys are likely to have temperature limitations that may restrict their application. The lower application temperatures for these could therefore affect overall power plant efficiency (Huenert and others, 2009). Other studies are addressing possible carburisation effects (the formation of metal carbides in a material resulting from exposure to a carbon-containing atmosphere). Studies suggest that the reaction between some Cr steels and CO₂ can result in carburisation occurring between 500°C and 620°C. Carburisation has been found to be influenced by several factors that include the oxygen partial pressure, the Cr content of the individual steel, and the makeup of the flue gas (moisture, sulphur, etc). However, a number of important materials-related areas remain under investigation. For instance, it is not yet clear if carburisation impacts on the mechanical reliability of components – long-term creep behaviour in oxyfuel atmospheres is not yet understood (Kranzmann and others, 2011). Fatigue testing will be required to address this.

As part of an extensive programme being carried out in the USA examining PCC oxyfuel retrofit applications, NETL has identified several major materials performance research areas. These are fireside corrosion within the boiler, steam turbine oxidation, supercritical CO₂ pipeline corrosion, and corrosion involved in a NETL-developed CO₂ capture method (Integrated Pollutant Removal – IPR). In the area of fireside corrosion, testing is comparing air and oxyfiring at temperatures expected to result in the highest fireside corrosion rates (675–700°C). The effect of sulphur levels in the gas and ash paths is being addressed; higher levels are expected to increase corrosion rates and may therefore require the use of more corrosion resistant alloys or coatings. Data suggests that increased sulphur in the coal ash maybe more important to fireside corrosion than increased sulphur in the gas phase. This fireside boiler corrosion research forms part of the US contribution to a US-UK collaboration on advanced materials for clean coal technology supported by the UK Department of Energy and Climate Change (DECC) and the US DOE.

As part of the NETL-led programme, a study to determine the effect of oxy-combustion on boiler tube corrosion was undertaken by Foster Wheeler North America Corporation. The main objectives were to compare the corrosion characteristics of oxy- and air-based combustion, identify the corrosion mechanisms involved, determine their effects on conventional PC boiler tube materials, and evaluate the suitability of alternative/advanced materials for this new mode of combustion. As part of the programme, test coupons of conventional and advanced boiler tube materials were coated with

deposits and exposed to different oxy-combustion flue gases for up to 1000 hours. The analysis of the test coupons (under way) suggests that the effect of oxy-combustion can vary with the material, type of deposit, and temperature, with wastage tending to increase with rising temperature, especially under strongly reducing conditions. Higher chromium levels appear to reduce impacts. Data so far suggests that the material losses observed from oxy-combustion induced corrosion should not be a problem in most PC boiler retrofits, provided that bulk gas SO₂ levels do not exceed 3200 ppm (Robertson and others, 2011).

Other US studies have been examining the corrosion rates of boiler waterwall and superheater materials (such as T22, P91 and 347H) while firing high sulphur bituminous and PRB sub-bituminous coals under both air firing and oxyfuel conditions. It has been determined that for all coals tested, waterwall corrosion rates were lower (compared to air firing) under oxyfuel conditions. This decrease in the rate of corrosion on heat transfer surfaces when retrofitting for oxy-combustion could be an important advantage for the technology. However, under other conditions, superheater corrosion rates were found to increase slightly. Corrosion rates for some lower alloyed materials were shown to increase significantly during transients from reducing to oxidising conditions when air firing, and from oxidising to reducing conditions when oxy-firing. Such transients may contribute to practical in-plant corrosion rates in the near-burner and near-overfire air port regions (Frya and others, 2011).

In Europe, several studies are addressing the limits of materials for use in high efficiency oxyfuel coal plants, with particular emphasis on possible corrosion issues. For instance, a collaborative EU-funded project involving IFRF, ENEL, IFK, Alstom Power Systems, Vattenfall, Outokumpu Stainless, and Swerea Kimab is examining boiler corrosion under oxy-fuel conditions.

6.1.2 Improved oxygen production

A major requirement for oxyfuel systems is a reliable supply of high purity oxygen. Although deployed commercially within a number of industrial sectors, oxygen production carries with it significant cost and energy implications. Thus, a major area for improving the effectiveness and application of oxyfuel technology is the provision of lower cost oxygen. Currently, the systems encountered most widely are based on the use of a cryogenic air separation unit (ASU). There are only limited possibilities for reducing the associated costs and reducing the power requirements of these.

For the first tranche of large-scale oxyfuel demonstrations and the first commercial plants, cryogenic air separation will be the only viable technology available. However, in the longer term, other air separation technologies based on membranes or adsorbents are seen as potential candidates (ZEP, 2010a). Specific energy consumption of today's cryogenic processes is in the range 160–220 kWh/t; longer-term R&D aims to reduce this to 120–140 kWh/t for improved cryogenic processes and 90–120 kWh/t for membrane or sorbent-based technologies. Such advances will also benefit oxygen-blown IGCC facilities.

The GCCSI and other organisations have recently highlighted the need for further RD&D and the development of novel oxygen production techniques with the potential to decrease costs (Global CCS Institute, 2009; EPRI, 2012). However, only a relatively small number of projects are dedicated solely to this. Currently, although still some way from commercial deployment, the most developed alternative appears to be Air Products' Ion Transport Membrane (ITM) system. This is a compact single stage process that produces high purity oxygen. ITM technology uses a ceramic material that, under temperature and pressure (800–900°C, >1.4 MPa), ionises and separates oxygen molecules from the air. Membranes are highly selective and provide fast transport for oxygen (Steele and others, 2010). No external source of electrical power is required in the process. The technology has the potential to produce oxygen more economically and efficiently, decrease the oxygen plant footprint, and decrease the cooling water requirement for most large oxygen demand applications. A multi-

phase project involving NETL, Air Products, EPRI, and other partners is under way in the USA. As part of this, Air Products is in the process of building a new 100 t/d ITM pilot- (TRL-7) scale oxygen production test facility in Louisiana. This is a scale-up (times twenty) of an existing smaller development unit. The plant will include both an ITM unit producing oxygen and an electrical cogeneration unit (5 MWe) generating power. The project is being funded in part by the US DOE and is scheduled to be operational in the second half of 2012 (Air Products, 2011). It is anticipated that the programme will provide reliable engineering and economic data allowing for further scale-up to a 2000 t/d plant (TRL-9).

Several other promising technologies are also being pursued:

Praxair is developing a system based on the use of an oxygen transport membrane (OTM) within the boiler. At high temperature, oxygen diffuses across this ceramic membrane. In 2010, the company was awarded a US\$35 million US DOE grant to accelerate development of the technology. It is claimed that the OTM system has the potential to reduce the parasitic power requirement for the ASU. The system utilises the large gradient in oxygen partial pressure between the fuel and airside of the OTM to drive oxygen transport through the membrane. By utilising a chemical driving force for air separation, very little power is consumed for air compression and the parasitic power consumption required for oxygen production is reduced by 70–80%, compared to that of a cryogenic ASU.

In a co-operative agreement with the US DOE, Praxair is developing and scaling-up the OTM technology towards pilot-scale testing. The project has two phases. Phase I will focus on materials development, process, economic modelling, and technical feasibility studies (Wilson and others, 2010). Praxair will then select an optimum process configuration for OTM integration into a coal-fired power plant. Phase II will develop basic engineering design and costing of major system components and produce a plan for pilot testing of the technology. Currently, Praxair and Shaw Energy & Chemical are collaborating on the construction of a 7.5 MWth pilot-scale test and development facility. This will produce 5 t/d of oxygen (Kelly, 2011).

An alternative system known as Ceramic Auto-thermal Recovery (CAR) is being developed by the **Linde Group/BOC**. The process uses the oxygen storage properties of perovskites to adsorb oxygen from air in a fixed-bed, then release the adsorbed oxygen into a sweep gas, such as recycled flue gas, that can be fed to the furnace. In the process, oxygen is separated from an air stream using a perovskite ceramic oxide adsorbent (composed of lanthanum, strontium, cobalt, and iron) at high temperature (800–900°C). Preliminary design and economic assessment of the CAR process for integrated high temperature oxygen production in oxy-combustion systems suggests that this approach offers promise for reducing capital cost and power consumption, assuming performance targets can be achieved. Perovskite material development for the process has been progressed with European partners and received funding under the EU 6th Framework programme. In order to validate the process, pilot scale testing is being carried out (Krishnamurthy and others, 2007). There are longer term plans for the development of a 9 t/d O₂ production plant (TRL-6).

There are also various other routes towards lower cost oxygen production being pursued by a number of US DOE-sponsored projects. For instance, **Eltron Research** is designing and developing a temperature swing adsorption (TSA) based system capable of producing high purity (>99%) oxygen. Another leading technology being developed is Chemical Looping Combustion (CLC), in which oxygen is separated from nitrogen via a reversible reaction with suitable solids that are then transferred to a ‘combustor’ where the solid-oxygen reaction is reversed, the fuel burned, and the resulting CO₂ produced as a concentrated gas stream (EPRI, 2012). Currently, bench-scale activities are ongoing to identify suitable solids. Process development units are being constructed for developing solids handling schemes and to characterise the performance of candidate solids and processes.

6.1.3 Combined SO₂ and CO₂ capture systems

The flue gas from oxyfuel combustion generally comprises mainly water vapour, CO₂, SO₂ and small amounts of other impurities. Most oxyfuel carbon capture systems being developed aim to remove CO₂ and SO₂ in separate stages; SO₂ is removed by an FGD process and CO₂ captured using a solvent scrubbing stage. However, ongoing RD&D is examining possible ways to combine both processes in a single step. In the USA, Bechtel is developing an oxy-combustion technology with the aim of combining these. A similar system has been proposed by Air Liquide (Santos, 2012). This is unlike, for instance, the FutureGen 2.0 project proposed for Meredosia, where the flue gas treating systems will remove each individual impurity separately. NO_x will be removed by an SCR system, SO₂ removed by an FGD, and CO₂ removed by cryogenic separation. Some compression systems within a cryogenic CPU are claimed to also remove NO_x (Oettinger, 2012c).

A major goal of combining CO₂ and SO₂ removal in a single system is to reduce costs and simplify plant design. Bechtel's combined removal process is based on the principle that each has a different liquefaction temperature, hence can be separated using fractionation techniques (a system used commonly to separate different hydrocarbon fractions in refineries). With Bechtel's proposed technology, CO₂ would be produced as a supercritical fluid capable of meeting pre-determined SO₂, moisture and oxygen limits for either industrial or underground injection applications. Advantages claimed for the combined SO₂/CO₂ process include:

- elimination of the need for a lime or limestone-based FGD. By eliminating the need for a wet FGD, cost and energy savings could be achieved;
- the energy required to separate both SO₂ and CO₂ should be almost the same as that of separating CO₂ only;
- SO₂ would be removed as a cold liquid product that can be transported in vessels and is a saleable product;
- CO₂ purity can be controlled to meet the final product applications;
- the process would generate no desulphurisation waste products, and would simplify flue gas treatment from fossil fuel power plants.

However, to date, only small scale testing has been undertaken and the system requires demonstrating at a larger scale (Wen and Kimtantas, 2011). Various technology developers such as Bechtel, Babcock & Wilcox, and Air Liquide are continuing research into different plant designs that optimise carbon capture in different oxy-combustion models.

6.1.4 Development of pressurised oxyfuel combustion systems

Oxyfuel combustion systems operating under pressure potentially offer some advantages over non-pressurised equivalents. So far, pressurised oxy-combustion process development has been carried out at the 5 MWth level. Recent research has indicated that pressurised systems have the potential for better performance than 'conventional' atmospheric oxy-fuel combustion power cycles. Various studies suggest that pressurised systems could provide a number of advantages (Benelli, 2011; Ditaranto, 2011; Vitalis, 2011; EPRI, 2012). These include:

- an increase in heat recovery from the flue gas – process pressure has a significant impact;
- saving in compression work – process pressure has a small effect on the overall compression work associated with O₂ and CO₂ compression;
- at pressure, water vapour condenses at temperature high enough for latent heat to be recovered in the steam cycle, leading to improved efficiency;
- reduced size and cost of system components such as boiler;
- absence of air-leakages into the system (although conversely, there could be the risk of CO₂ release where the installation is not airtight);
- the capability of burning inexpensive coals;
- the CO₂ generated is partially compressed. At pressure, CO₂ can be condensed to liquid, saving

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- power by pumping liquid instead of compressing gas;
 - lower flue gas recirculation specific work;
 - high levels of CO₂ purity are viable;
 - heat transfer coefficients in a pressurised (1 MPa) convective boiler are expected to be an order of magnitude higher than those of convective sections of conventional boilers.

Studies carried out by Hong and others (2008, 2010) suggest that for a proposed Rankine cycle, the use of a pressurised oxyfuel power cycle with carbon capture would increase the net efficiency from 31.5% to 34.9% (LHV). The optimal pressure for this cycle would be around 1 MPa, due mainly to the fan compression work driving the flue gas recirculation (Ditaranto, 2011). Under these conditions, in terms of the thermal energy recovery and gross power output, an oxyfuel combustion power cycle utilising a pressurised coal combustor would achieve better performance than an atmospheric pressure equivalent. It was considered that pressurisation would enable the system to recover more thermal energy from the flue gases and avoid the need for high-pressure and low-pressure steam bleeding. Because of the raised dew point and the higher available latent enthalpy in the flue gases, it would be possible to recover a large amount of high-pressure water-condensing flue gas thermal energy. By recuperating more thermal energy from the flue gases to generate steam, the system would be able to eliminate steam bleeding and to use more steam in the turbines. As a result, a pressurised oxyfuel power cycle would produce an overall increase in gross efficiency, compared to an atmospheric combustion pressure equivalent.

To date, only limited RD&D has been carried out in the area of pressurised oxyfuel systems. However, their potential is being explored by several technology developers. For instance, in Italy, work being undertaken by ENEL suggests that oxyfuel combustion at high pressures would increase the burning rate of char and the heat transfer rates in the convective sections of the heat transfer equipment. To demonstrate these benefits, for several years, ENEL has been developing and testing a patented pressurised coal combustion technology (ISOTHERM). This has been tested at a scale of 5 MWth (TRL-5), operating at 4 MPa. The technology is claimed to generate a CO₂ stream of high purity with lower energy penalties than conventional systems.

In the USA, Babcock-Thermo Carbon Capture LLC (a joint venture between Babcock Power and Thermo Carbon Capture) is developing an integrated CO₂ and multi-pollutant capture boiler system, based on pressurised oxy-combustion (ZEBS – Zero Emission Boiler system). Advantages claimed for the ZEBS technology include higher efficiency (compared to ambient oxyfuel, post-combustion capture, and IGCC + CCS), lower CAPEX for coal-based generation with CCS, and the lowest cost of generation with CCS. The technology is also claimed to generate electricity more cheaply than most renewable energy sources. Other advantageous features include suitability for new-build and retrofit applications, applicability to any steam cycle (including double reheat), capture of all pollutants, and avoidance of air in-leakage. Furthermore, the system delivers liquid CO₂ at ambient temperature (no chilling is necessary), requiring only pumping, not compression, for pipeline transport.

Phase I of the development programme to establish the underlying science and thermodynamics has now been completed. This has included comprehensive modelling and process design; a design for a 600 MW plant has been produced and used to compare system cost and performance with competing technologies. Phase II is now under way, focused on the design, construction and operation of a small-scale pilot plant. Reportedly, the joint venture is in advanced negotiations for the pilot plant and in discussions with major utilities to advance the ZEBS technology (Vitalis, 2011). Pilot plant operations would be used to demonstrate all aspects of the system, validate design standards for larger plants, provide data on operability, allow for process optimisation, and provide a system for process enhancements.

Also in the USA, ThermoEnergy Corporation and ITEA S.p.A. of Italy are collaborating to promote, finance, design and construct a 50 MW pilot plant and a 320 MW commercial facility using pressurised oxy-combustion. The technology is being aimed primarily at coal-fired plants. The system

is being developed and marketed by Unity Power Alliance LLC, a joint venture between ITEA and ThermoEnergy. Unity Power expects to begin building the 50 MW plant in 2013; this will provide data on scaling-up the technology for the commercial power plant. It is claimed that the technology is capable of responding flexibly and quickly to changes in demand, going from 10% to 100% of its generating capacity in 30 minutes.

Elsewhere, a novel system is being developed by Net Power, Toshiba, power producer Exelon, and the engineering firm Shaw. The new technology makes use of plant exhaust by directing part of the CO₂ in the exhaust stream back into a gas turbine, eliminating the need for a steam turbine; this helps offset the cost of the oxygen separation equipment. The technology was originally conceived to work with gasified coal, although the company is planning to demonstrate it first with natural gas. Shaw is funding a 25 MW demonstration power plant that is scheduled to be completed by mid-2014. It is claimed that the system will have an efficiency of more than 50%. Net Power plans to sell the captured CO₂ for EOR. However, process economics will need to be confirmed.

In Canada, technical and economic studies carried out by CANMET suggest a net efficiency gain and reduction in the capital cost and the cost of electricity when using high pressure oxyfuel combustion. A high pressure oxyfuel process (HiPrOx) has been proposed and evaluated (CANMET, 2008). This capitalises on the advantages provided by operation at elevated pressure and uses mostly off-the-shelf industrial components (furnaces, steam/gas heat exchangers, air separation units, and pumps, etc). Comprehensive technical and economic feasibility studies of the HiPrOx technology concluded that compared to non-pressurised systems:

- boiler efficiency was increased by ~10%;
- steam cycle efficiency was increased by ~8% due to heat duty savings at feedwater heaters;
- auxiliary power consumption was reduced by ~35%;
- improved fuel burnout;
- furnace and heat exchanger sizes were significantly smaller;
- HiPrOx cycle efficiency was less influenced by high moisture fuels (such as lignite, biomass);
- air pollution control effectiveness was increased;
- scrubber and flue gas condenser size was reduced;
- capital and operating economics were better than existing power generation with CCS.

CANMET plans to develop and test the technology to at least pilot scale through collaboration with other organisations.

Pressurised oxyfuel circulating fluidised bed combustion

Most development efforts have so far been directed towards PCC-based applications. However, pressurised oxyfuel circulating fluidised bed combustion is also being actively considered. Increasingly, oxygen-enhanced CFB-based combustion is being viewed as an effective route to improving energy efficiencies and providing near-zero emissions power production. All the established advantages of conventional CFBC are transferable to oxyfuel CFBC. However, compared to oxyfuel PCC boilers, oxyfuel CFBC could provide several additional advantages (CANMET, 2010):

- the technology requires significantly less recycled flue gas to control boiler temperature due to the recirculating solids – these effectively act as a heat moderator. This allows higher oxygen concentrations to be used in the combustor and improve process economics (compared to PCC-based systems) through a reduction of the size of the CFBC boiler island by as much as 50%. This will also ease scaling-up of the technology;
- sophisticated burner systems are not required as the bulk of the heat transfer is accomplished with solids;
- there is no requirement for significant alterations to heat exchange components, as needed in oxyfuel PCC boilers;
- biomass can be cofired at any level, making it possible to offer net reductions of anthropogenic CO₂ emissions.

7 Summary and conclusions

The report provides a description of the three main carbon capture approaches (with the potential for deployment on coal-fired plants) currently the focus of most research and development. These comprise pre-combustion capture from syngas produced in IGCC and gasification plants, post-combustion capture using different solvents, and oxy-combustion technology. As these systems have been reported widely elsewhere, only brief process descriptions are provided. So-called breakthrough technologies and conceptual designs at early stages in their development or still at very small scale are not discussed in this report.

The report has sought to provide an update of the larger scale activities taking place within the three main carbon capture routes currently being pursued for application to coal-fired power plants. For each family of technologies, where possible, outstanding gaps in the knowledge, and measures to address these, have been identified. However, in some cases, issues of commercial confidentiality have meant that detailed requirements have not made public by the technology developers, hence only general conclusions can be drawn on the technological challenges remaining and commercial RD&D activities under way.

At present, both pre- and post-combustion capture technologies are commercially available and are used widely for purifying gas streams in a variety of industrial processes. There are also a handful of small coal-fired power/cogeneration plants that capture a portion of the CO₂ present in boiler flue gases and utilise it directly or sell it on for different commercial purposes. For both systems, a broad spectrum of RD&D activities is under way, aimed largely at eventual large-scale deployment. Oxy-combustion capture is still under development and is not currently a commercial proposition, although recent developments undertaken by Vattenfall in Germany have helped push the technology much further forward. A further boost is expected once the Callide project in Australia progresses beyond commissioning. The advantages and limitations of each of the three main technologies are discussed in the report, along with plans for their continued development and demonstration, predominantly in large-scale power plant applications.

Potentially, all three carbon capture approaches are capable of high CO₂ capture efficiencies, typically about 90%. However, for each, the major drawbacks associated with current processes are their high cost and substantial operational energy requirements. A considerable proportion of the ongoing and planned research and development is dedicated firmly to reducing process costs and associated energy penalties.

Pre-combustion capture projects are focused on both coal-based IGCC and non-IGCC applications. In the case of IGCC + CCS, there are projects ongoing or being developed in The Netherlands, Spain, USA, Japan, China and the UK. Various pilot-scale projects are addressing a range of objectives that include enhanced process integration and further hardware and catalyst development. Although some projects are still in their initial stages of development, others are beginning to produce useful data that is being fed into programmes aimed at reducing process costs, minimising the associated energy penalty, and enhancing scaling up activities. Non-IGCC projects that feature carbon capture are also reviewed. These include the production of chemicals, SNG and liquids from coal.

Post-combustion capture using solvents such as methanolamine is commercially available and has long been used for various industrial applications. However, such capture processes were not designed specifically for application to large coal-fired power stations. Consequently, the necessary equipment may be sizable, steam demand high, and contaminants in the flue gas may affect the effectiveness of the capture process. Despite this, post-combustion capture is viewed as having the greatest near-term potential for reducing CO₂ emissions, as potentially, it could be retrofitted to many existing coal-fired power plants. Many possible technology variants and options are being followed and major development programmes are under way in Europe, North America, and the Asia-Pacific region.

Globally, there are a number of promising technologies that have now progressed to at least small pilot-scale operations. As with other systems, for post-combustion capture, the major challenges revolve around the relatively large parasitic load that the process imposes on a power plant; a significant portion of current RD&D is focused directly or indirectly on this issue. Areas flagged up that merit further RD&D include improved integration of the capture system with the power plant, and the development of novel/improved solvents and plant hardware. Attention is also required to address possible issues concerning the commercial scale supply of some more specialised solvents, and concerns over possible environmental impacts of amines. There may also be materials issues associated with some of the latter, although this is not a concern for systems that use ammonia.

Oxyfuel technology is essentially an adaptation of existing components and sub-systems to a new application; most of the latter already exist. Furthermore, test results from pilot projects appear to be confirming the robustness of the technology. It is currently undergoing rapid advancement, with the development of a number of pilot/demonstration projects proposed or under way in Europe, North America and the Asia-Pacific region. Industrial-scale testing of coal combustion and burners is being conducted by several technology vendors. However, the technology holds potential for further improvement. The most compelling need (and a major focus of R&D) is for the development and application of improved, lower-cost systems capable of delivering large quantities of high-purity oxygen; in current oxyfuel schemes, this is the major cost item. Ion Transport Membranes and other novel techniques for lower-cost O₂ production are being developed and are expected to be available within the next decade. These hold the potential for significant process cost reduction. Some of the challenges and development activities under way are similar to those being developed for both post- and pre-combustion capture. Most focus on cost reduction, reduction of energy requirements, and demonstration of integrated operation at larger scale.

Oxyfuel combustion is viewed as being potentially suitable for application to both new-build power plants and retrofit situations. Oxyfuel combustion capability and CO₂ capture is technically straightforward when considered during the initial design of the power plant. For retrofits, only moderate modifications to the power plant would be required for the future conversion to oxyfuel combustion. Thus, it appears technically possible to convert at least some non-capture-ready plants to oxyfuel combustion, although the performance would not be as good as that of a new high efficiency plant featuring an optimised oxyfuel CCS solution. However, this would be normal for retrofit scenarios and would also be the case with post-combustion.

Even with an aggressive development schedule, the general consensus is that (assuming they prove successful) the three main approaches to CO₂ capture are unlikely to become commercially available for large-scale deployment on coal-fired power plants for some time. Most technology roadmaps anticipate that CO₂ capture will be available for commercial deployment on power plants by 2020 or after. Processes considered to be at a relatively advanced pilot stage are based mainly on new or improved solvent formulations (such as ammonia and advanced amines/blends) currently undergoing testing and evaluation. Should larger scale testing confirm their overall benefit, such advanced solvents could be available for commercial use within several years. However, in some cases, widespread application could create supply bottlenecks. In the case of pre-combustion capture, several coal-fuelled IGCC + CCS projects are under way, with others planned or under development. Oxy-combustion processes also are being tested and evaluated at large pilot plant scale with a view to scaling up the technology.

As noted above, a major issue with all forms of CO₂ capture system is both capital and operating cost. However, based on previous experience with the introduction of other forms of environmental control technology on coal-fired plants, associated costs tend to reduce over time. For instance, after an initial rise during the early commercialisation period, the cost of post-combustion SO₂ and NO_x control systems declined by 50% or more after about two decades of deployment at coal-fired power plants (Folger, 2010). It is therefore considered that once these CO₂ capture technologies become deployed widely, a similar downward trend might be expected.

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Appendix – Technology Readiness Levels (TRL)

One method of describing the maturity of a technology or system is the scale of technology readiness level (TRL). These were initially developed for NASA and subsequently adopted by the US Department of Defense and other organisations involved in developing and deploying complex technologies or systems, both in the USA and elsewhere. More recently, the system was taken up by EPRI to describe the status of new carbon capture technologies. The TRL system has also been adopted by the GCCSI.

The achievement of a given TRL helps to identify the resources required to achieve the next level of readiness. An achievement of TRL-9 indicates that the first successful operation at a scale normally associated with commercial deployment has been achieved. Progressively higher technical and financial risks are required to achieve the TRLs up to and including TRL-9 (GCCSI, 2011). However, the system does not address the commercial or economic feasibility of deploying the particular technology; it is not intended to express overall project development risk. This is project-specific. The GCCSI suggests that for the purposes of a TRL assessment of advanced coal technology, TRL-9 would be achieved by a power plant in the capacity range 400–800 MW (net).

However, the TRL system is not accepted by all bodies. For instance, the CSLF considered its application to major CSLF-recognised projects and after analysis of the data, determined that performing such an analysis would be subjective, complex, the results would be argumentative and difficult to interpret, and that the end product would not be useful or helpful in contributing to the existing analysis available on the projects. It was therefore decided not to pursue further the analysis of CSLF projects through use of a TRL methodology (Giove, 2011).

Technology Readiness Level (TRL)	Description	Specifically for CCS systems – NASA (Folger, 2010)	As defined by GCCSI
1	Basic principles observed and reported	Conceptual design – this stage is one for which the basic science has been developed, but no physical prototypes yet exist. May be developed and tested with computer models before any laboratory work is done. This allows for confirmation that the design principles are sound, plus some degree of process optimisation before progressing to next stages	Basic principles observed
2	Technology concept and/or application formulated		Application formulated
3	Analytical and experimental critical function and/or characteristic proof-of-concept	Laboratory- or bench-scale – represent the early stage of process development in which a process is first successfully constructed and operated in a controlled environment, often using materials and test gases to simulate a commercial process or stream (such as a flue gas stream)	Analytical, ‘proof of concept’
4	Component and/or breadboard validation in laboratory environment		Laboratory component testing
5	Components and/or breadboard validation in relevant environment		Component validation in relevant environment
6	System/sub-system model or prototype demonstration in a relevant environment	Pilot plant-scale – represent an initial demonstration stage and corresponds to levels 6 and 7. This stage is where a process or technology is tested in a realistic environment, but at a scale that is typically one to two orders of magnitude smaller than the full-scale demonstration. Data are gathered to refine and further develop a process, or to design a full-size (or intermediate size) demonstration plant	Process development unit (0.1–5% of full-scale)
7	System prototype demonstration	Full-scale demonstration plant – corresponds to levels 7 and 8. It represents the stage at which a CO ₂ capture technology is integrated into a full-size system in order to demonstrate its viability and commercial readiness in a particular application. The term full-scale is flexible, but in general would correspond to a gross power plant size of ~250 MW, with a corresponding CO ₂ capture rate of ~1–2 Mt/y for a coal-fired plant	Pilot Plant (>5% commercial-scale)
8	Actual system completed, tested and demonstrated		Sub-scale commercial demonstration plant (>25 per cent commercial-scale)
9	Actual system proven through operation	Commercial Process - a commercial carbon capture technology or process that is available for routine use in a particular application such as a power plant. The capture technology is offered for sale by one or more reliable vendors with standard commercial guarantees. This is the maturity level that utilities will normally require before installing a CCS system at a US power plant	Full-scale commercial deployment