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Assessing the Cost Reduction Potential and Competitiveness of Novel (Next Generation) UK Carbon Capture Technology

Literature Review

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Report for

Department for Business, Energy & Industrial Strategy

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1 Introduction

The Department for Business, Energy and Industrial Strategy (BEIS) has commissioned Wood to carry out a study to assess the cost reduction potential and competitiveness of novel (Next Generation) UK carbon capture technologies.

The aim of the overall study is to evaluate the most promising UK-led CO₂ capture technologies for the Power and Energy Intensive Industries in order to inform UK innovation spending programmes and define future CCS policy. The study objective is to gather information on prospective next generation technologies and perform a techno-economic assessment of the potential cost reduction and competitiveness of these technologies in comparison with current state-of-the-art technology. CO₂ transportation and storage is not within the study scope.

The first stage of the overall study was to conduct a literature review covering the full range of applicable carbon capture technologies, starting from the list contained in the IEAGHG Report “Assessment of Emerging CO₂ Capture Technologies and their Potential to Reduce Costs”, 2014/TR4, December 2014, but also covering more recent developments. The approach used was to search on-line for updates relating to the IEAGHG report included technologies on the relevant company, research institution or government body websites (such as the US Department of Energy), and in academic journals via Science Direct. Further references were also kindly supplied by BEIS and members of the Project Advisory Board.

This report provides a summary of the reviewed public domain articles and relevant websites that were assessed for the literature review with a particularly emphasis on determining the current technology readiness level of each technology, or group of technologies.

In the IEAGHG Report, the development of emerging technologies is assessed on a nine-point numerical scale of Technology Readiness Level (TRL) based on the descriptive definitions proposed by the Electric Power Research Institute (EPRI). These are summarised in Table 1-1.

Table 1-1: Technology Readiness Level (TRL), from the IEAGHG Report “Assessment of Emerging CO₂ Capture Technologies and their Potential to Reduce Costs”, 2014/TR4, Dec 2014

Demonstration	9	Normal commercial service
	8	Commercial demonstration, full scale deployment in final form
	7	Sub-scale demonstration, fully functional prototype
Development	6	Fully integrated pilot tested in a relevant environment
	5	Sub-system validation in a relevant environment
	4	System validation in a laboratory environment
Research	3	Proof-of-concept tests, component level
	2	Formulation of the application
	1	Basic principles, observed, initial concept

The literature review forms a relatively small part of this study and it is likely that some references or technologies have not been included, or that key information on those technologies was not available in the public domain at the time of writing. Thus, this should not be assumed to be an exhaustive list of promising CO₂ capture technologies.



2 Post-Combustion Capture

2.1 Overview

Post-combustion CO₂ capture refers to capture of carbon after combustion has taken place, i.e. from flue or exhaust gas. However, the definition of post-combustion CO₂ capture can also include CO₂ capture from other sources which are similar in nature to a flue gas, for example off-gas from cement manufacture.

The 2014 IEAGHG report has given each of the post-combustion capture technologies researched in this literature review a Technology Readiness Level (TRL). Further development has been conducted for many of these technologies since that time. The following table summarises TRL's given to each technology by the IEAGHG in 2014 alongside the 2017 TRL estimated by Wood, resulting from our literature review.

Table 2-1: TRL for Post-Combustion Capture Technologies

Technology	2014 TRL	2017 TRL
Conventional Solvents	9	9
Improved Conventional Solvents	6-8	6-8
Encapsulated Solvents	1	2-3
Precipitating Solvents	4-5	4-5
Biphasic Solvents	4	4
Ionic Liquids	1	1
Algae Based Capture	1	3
Polymeric Membranes	6	6
Polymeric Membranes / Cryogenic Separation Hybrid	6	6
Room Temperature Ionic Liquid (RTIL) Membranes	2	2
Vacuum Pressure Swing Adsorption (VPSA)	3	3
Temperature Swing Adsorption (TSA)	1	7
Molecularly Imprinted Polymer Particle CO ₂ Sorbents *	-	1-2
Enzyme Catalysed Adsorption	1	6
Amine Catalysed Adsorption *	-	6
Electrochemically Mediated Adsorption	1	1
Mineral Carbonation *	-	5
Cryogenic Capture	3	4
Supersonic Inertia Capture	1	3

* These technologies were not assessed in the IEAGHG 2014 report.

2.2 Solvents

2.2.1 Conventional Solvents for Post-Combustion CO₂ Capture

Post-combustion CO₂ capture using amine based solvents is a conventional method of producing CO₂ for industrial and beverage uses with the main licensors of the processes having had reference plants in operation for many decades. These plants are mostly at an order of magnitude (or more) smaller than that which would be required for capturing 90% of flue gas from a utility



scale power plant. However, all of these licensors have been investing in improving their solvents and processes in order to compete on the scale required for CCS on utility scale power applications. The main licensors are:

- Shell (Cansolv Process)
- MHI (KM CDR Process)
- Fluor (Econamine FG+)
- Kerr-McGee/ABB Lummus
- Siemens (Post-CAP)
- Dow (DOW Amines)

The largest demonstration plants for post combustion CO₂ capture are all based on conventional, proprietary amine based solvents, these are at Boundary Dam coal power plant in Canada, using Shell's Cansolv process capturing 1 million tonnes per annum (MTPA) of CO₂ and Petra Nova coal power plant in the USA, using MHI's technology to capture 1.4 MTPA of CO₂.

1. *Howard Herzog, MIT, "An Introduction to CO₂ Sequestration and Capture Technologies", August 1999.*
https://sequestration.mit.edu/pdf/introduction_to_capture.pdf

Fluor's largest post-combustion CO₂ capture plant was operated on gas turbine flue gas capturing 320 thousand tonnes per annum (kTPA) of CO₂ running at Bellingham, USA, from 1991 until the power plant moved to peak shaving mode in 2005. Kerr-McGee's largest plant produces 800 kTPA of CO₂ captured from a coal boiler. Dow's largest operating plant captures 160 kTPA from an ammonia plant reformer, although Dow used to operate a 1.2 MTPA plant capturing CO₂ from a gas boiler which closed prior to the turn of the century.

Most, if not all, of the above licensors have been involved in development of designs for full scale (300MW+) CCS demonstration projects at either Pre-FEED or FEED level, for example Fluor developed a FEED design for the ROAD project, MHI for the Kingsnorth Project and Shell for the Peterhead project.

As a technology group, conventional solvents can be considered as TRL-9.

2.2.2 Improved Conventional Solvents

The technology grouping of improved conventional solvents covers a wide range of technologies. Overall, Wood judges these technologies to remain within the range of TRL-6 to 8 since any commercialised schemes are yet to reach normal commercial service at power plant scale.

2. *IEAGHG 'Assessment of Emerging CO₂ Capture Technologies and their Potential to Reduce Costs', December 2014*

Conventional solvents are typically solvents based on amine derivatives. The IEAGHG report lists different amine based solvents that have been developed, such as monoethanolamine, 2-amino-2-methyl-1-propanol (AMP), diethanolamine, etc. The IEAGHG selects seven factors that it believes are important to be considered when developing a solvent for CO₂ absorption. The paper goes on to discuss the focus of the research for developing conventional solvents in relation to each of these seven factors. These factors are:

- Absorption capacity
- Absorption rate
- Energy for regeneration
- Degradation
- Corrosion
- Environmental impact



- Solvent cost

The paper states that there are several solvent based pilot plants and demonstration projects in operation / construction / planning around the world, and that these pilot plant operations have successfully demonstrated the applicability of the amine based CO₂ absorption process. However, the report does not mention any of these projects by name.

3. *Jorgen Norklit Jensen, 'Experience with the CASTOR/CESAR Pilot Plant: Workshop on Operating Flexibility of Power Plants with CCS, Imperial College, London, Dong Energy Power, 2009*
http://ieaghg.org/docs/flexibility%20workshop/14_Flexibility%20workshop%20Jensen.pdf

These slides introduce the CASTOR pilot plant at Esbjerg power plant. The aim of the project is to commercially prove industrial post-combustion CO₂ capture amine processes for a coal fired power plant.

The slides list several providers of the amine CO₂ capture technology. These include:

- ABB Lummus / Kerr-McGee
- DOW MEA / Flour Econamine FG: 30% MEA
- Mitsubishi Heavy Industries (MHI): KS-1 solvent

The plant is operated by Dong Energy and Vattenfall.

4. *Pierre LE THIEZ, 'CASTOR CO₂, From Capture to Storage PUBLISHABLE EXECUTIVE SUMMARY', IFP, 2008*

The report lists the project consortium. The following UK organisations and companies are listed:

- Imperial College (UK)
- E.ON UK (UK)
- Doosan Babcock (UK)

5. *Global CCS Institute:*
http://ieaghg.org/docs/flexibility%20workshop/14_Flexibility%20workshop%20Jensen.pdf

This website summarises the CESAR project (CO₂ Enhanced Separation And Recovery). The CESAR project is a follow-up project to the post-combustion capture work undertaken at the coal-fired Esbjerg pilot plant in Denmark under the CASTOR project that ended early in 2008. The objectives of continued pilot testing at the Esbjerg pilot plant under CESAR included evaluation of the potential for reducing energy consumption of CO₂ capture through advanced absorption / desorption process configurations at pilot scale and for reducing regeneration energy through use of novel amine solvents. Monitoring of actual solvent degradation, corrosion and emissions for the solvents tested also took place.

Modifications to the Esbjerg pilot plant were undertaken during 2008, after which a three-test campaign was conducted, covering a benchmark and two novel solvents:

- March-July 2009: 1000 hours using standard "30%-wt. MEA" solvent;
- November 2009-February 2010: 1000 hours with a blend of AMP and piperazine "CESAR 1";
- March-June 2010: 500 hours with 30%-wt. ethylenediamine (EDA) "CESAR 2". This campaign was shortened due to corrosion effects.

In another source, the UK organisations and companies listed as part of the CESAR project consortium are:

- E.ON (DE/UK)
- RWE (DE/UK)



- Powergen (UK)
 - Doosan Babcock (UK)
6. *Mr Peter van Os, 'CESAR Final Project Report, CO₂ Enhanced Separation and Recovery', CEASER Enhanced Separation and Recovery, 2011*
<https://setis.ec.europa.eu/energy-research/sites/default/files/project/docs/CESARFinalReport31May2012.pdf>

The results from the CESAR project concluded that the CESAR1 solvent performed better than MEA, and CESAR2 solvents were also tested. The benchmark MEA capture process with simplistic heat integration was calculated to incur costs of €42 - €68 per tonne CO₂ abated across the five base cases. The CESAR1 capture process with advanced integration was calculated to incur costs of €35 - €55 per tonne CO₂ abated.

The link below has downloads of numerous articles, papers and brochures related to the CESAR project:

<http://www.co2cesar.eu/site/en/downloads.php>

7. *Community Research and Development Information Service (CORDIS):*
http://cordis.europa.eu/project/rcn/107959_en.html

This web page provides an overview of the OCTAVIUS project. OCTAVIUS builds on previous CCS projects such as CASTOR and CESAR. The main coordinating research institutes and industrial partners of these projects also took part in OCTAVIUS. Results of the clean coal research are provided by end-users, engineering companies and technology vendors partnering in OCTAVIUS. Operability and flexibility of first generation post combustion processes are demonstrated by TNO, EnBW and ENEL pilot plants in order to prepare full scale demo projects such as the ROAD and Porto Tolle projects that were planned to start in 2015. In addition, OCTAVIUS was to include the demonstration of the DMX process on the ENEL pilot plant in Brindisi.

8. *Ferran de Miguel Mercader, Purvil Khakharia, Arjen Huizinga, Leanne Kester, Peter van Os and Earl Goetheer, 'Emission counter-measures in post-combustion CO₂ capture: Demonstration at pilot plant scale', TNO Gas Treatment, 2013*

This paper describes the acid wash that was designed for TNO's pilot plant as part of the OCTAVIUS project. One of the objectives of the OCTAVIUS project was the demonstration of emission countermeasures for post-combustion CO₂ capture. To accomplish this, an acid wash was designed and commissioned at TNO's CO₂ capture pilot plant, which was connected to a coal-fired power plant.

The project concluded that when using MEA as a solvent for post-combustion CO₂ capture, it is known that ammonia (NH₃) is produced by the reaction of dissolved oxygen with the amine (known as oxidative degradation). The ammonia is volatile and its emission must be controlled for health and environmental reasons. By first adding a water-wash on the top section of the absorber, the temperature of exiting flue gas can be controlled, reducing the emissions of ammonia and MEA. However, the emissions reduction from the water wash alone were not deemed sufficient and an acid wash was installed, which successfully reduced emissions.

A separate source names Doosan Babcock Limited and E.ON Technologies (Radcliffe) Limited as the UK participants in the project.

9. *Stepan Bazhenov, Alexander Rieder, Bernd Schallert, Vladimir Vasilevsky, Sven Unterberger, Evgeniia Grushevenko, Vladimir Volkov, Alexey Volkov, 'Reclaiming of degraded MEA solutions by electrodialysis: Results of ED pilot campaign at post-combustion CO₂ capture pilot plant', A.V. Topchiev Institute of Petrochemical Synthesis RAS, EnBW Germany, EON Technologies.*



This paper looks at a study completed as part of the OCTAVIUS project to evaluate the behaviour of heat stable salts (HSS) during electro dialysis reclaiming of MEA solvent (30 wt.% MEA). Amine-based solvents react with inorganic, acidic impurities in flue gases (SO₂, NO₂, HCl, etc.) to form heat stable salts decreasing the CO₂ capacity of amine. Since HSS cannot be regenerated in the stripper under normal operating conditions, continuous build-up of HSS in the solvent loop needs certain countermeasures, such as periodic thermal reclaiming at higher temperatures than the normal reboiler temperature. Electro dialysis is a mature membrane-based technology which is considered as a promising alternative approach. As a part of the OCTAVIUS project, electro dialysis reclaiming was demonstrated under real operating conditions at the post-combustion CO₂ capture pilot plant operated by EnBW AG and located at Heilbronn, Germany.

10. *Hanne M. Kvamsdala, Sören Ehlersb, Alfons Katherb, Purvil Khakhariac, Michiel Nienoordc, Philip Loldrup Fosbøld, 'Optimizing integrated reference cases in the OCTAVIUS project', SINTEF Materials and Chemistry, Hamburg University of Technology, TNO, Technical University of Denmark (DTU)*

This paper presents a process optimisation study that was performed during the OCTAVIUS project. Based on earlier projects, two reference power plants are modelled in Epsilon® Professional. The first is an 800 MWe coal case, the second a 430 MWe natural gas combined cycle (NGCC) case. For each power plant, two separate capture plants were considered: one using 30 wt% MEA as solvent system, the other with the CESAR1 solvent (a mixture of AMP and piperazine). This resulted in four different reference cases which were optimised by varying different process parameters and evaluating process modifications.

In a second step, the integration of the capture plant into the power plant was evaluated. This is important, especially for the coal fired power plant, where integration of waste heat from the capture plant or the CO₂ compressor intercoolers can lead to a significant increase in overall efficiency. The configuration of intercoolers for the CO₂ compressor was adapted to achieve the highest overall efficiency. For the natural gas combined cycle plant, integration was not so considered as beneficial, since there is no heat sink available in the water steam cycle.

In the end, the cost of electricity and cost of CO₂ avoided was calculated for all four cases. While the CESAR1 solvent system in a conventional absorber-stripper scheme is less costly (almost 17%) than the MEA solvent system in a process with Lean Vapour Compression (LVC) for the coal cases, the result is the opposite for the two NGCC cases, though the difference is not substantial. This work indicated that the benefits of energy integration options such as LVC, while attractive for MEA, are less applicable to the advanced amines.

11. *Jonathan Forsyth, Stuart Lodge, Stefano Consonni, Daniele Di Bona, Manuele Gatti, Emanuele Martelli, Roberto Scaccabarozzi, Federico Viganò, 'Evaluation of five alternative CO₂ capture technologies with insights to inform further development: 13th International Conference on Greenhouse Gas Control Technologies, GHGT-13, 14-18 November 2016, Lausanne, Switzerland', BP International Limited, Consorzio LEAP – Laboratorio Energia e Ambiente Piacenza, November 2016*

CCP have carried out a preliminary assessment on the potential of five alternative technologies suitable for post-combustion CO₂ capture from natural gas derived exhaust gases. The five cases included are:

- High-pressure solvent absorption from high-pressure exhaust gas from pressurised combustion / power generation;
- High-pressure solvent absorption supported by exhaust gas compression;
- CO₂ permeable membrane (see Section 2.3.1);
- Molten carbonate fuel cells (see Section 6.2);
- Supersonic flow-driven CO₂ deposition (see Section 2.5.2).



High-pressure solvent absorption from high-pressure exhaust gas from pressurised combustion / power generation

The paper states that this approach has been taken to tackle the low partial pressure of CO₂. The CCP used the system offered by Sargas as the starting point for their process modelling and cost estimating. In this process, the absorber is fed with exhaust gas from the gas turbine combustor where it is at relatively high pressure. In the CCP model, the gas turbine is split into a high to medium pressure section, from which the exhaust gases are fed to the HRSG then a hot potassium carbonate CO₂ removal process operating at 8 bar. The decarbonised flue gases are then re-heated and further expanded in a low pressure turbine.

High-pressure solvent absorption supported by exhaust gas compression

This process involves compressing exhaust gas to increase the partial pressure of CO₂ and help solvent absorption. The paper references the Partnering In Innovation process, which uses the physical solvent properties of pure water to absorb CO₂ from exhaust gas which has been compressed to 60 barg. Due to the necessary absorber height for this scheme, the absorption takes place in a 600m deep water-filled well. This exploits the hydrostatic pressure and uses a gas-lift pumping technique to circulate the water. The CO₂-lean exhaust gas is heated and then expanded in order to recover some of the mechanical power. Different integration options of such a capture technology with a combined cycle power plant were then assessed to maximise the energy recovery while limiting CO₂ emissions.

2.2.2.1 Carbon Clean Solutions Limited (CCSL)

12. *Mahdi Sharifzadeh, Prateek Bumb, Nilay Shah 'Carbon capture from Pulverized Coal Power Plant (PCPP): Solvent Performance Comparison at an Industrial Scale' Centre for Process Systems Engineering (CPSE), Imperial College London, Carbon Clean Solutions Limited, 2016*

This paper introduces a new methodology to assess the performance of CO₂ capture solvents. The problem is posed as retrofitting an existing pulverised coal power plant with post-combustion carbon capture using two solvents: CDRMax, a recently developed amine-promoted buffer salt (APBS) solvent by CCSL and MEA as the baseline solvent. The features of interest include model development and validation using pilot plant data, as well as integrated design and control of the capture process. The emphasis is on design and operation of the capture plant when integrated with the upstream coal-fired power plant, subject to variations in the electricity load. The results suggest that optimal design and operation of capture plant can significantly mitigate the energetic penalties associated with carbon capture from the flue gas, while providing effective measures for comparing solvent performances under various scenarios.

13. *Prateek Bumb, Ramesh Kumar, Purvil Khakharia, Earl Goetheer 'Demonstration of Advanced APBS Solvent at TNO's CO₂ Capture Pilot Plant', Carbon Clean Solutions Limited, TNO, 2014*

CCSL has developed a variety of energy efficient solvents and processes such as PCCMax, which aim to reduce the overall operating and capital cost of CO₂ capture. In collaboration with TNO, research and development considering aspects from fundamental properties, such as Vapour Liquid Equilibrium (VLE) concentrations, has been focused on developing energy efficient chemical solvents and addressing solvent management aspects such as solvent degradation, corrosion and emissions.

CCSL demonstrated their solvent technology at TNO's 6 TPD CO₂ capture pilot plant connected to a coal fired power plant from E.ON, Maasvlakte near Rotterdam. The advanced novel solvent APBS was compared with conventional solvents in terms of CO₂ absorption capacity, energy, cyclic capacity and absorption kinetics over 1000 operating hours. The APBS solvent was specifically developed to capture CO₂ from flue gas emissions from coal based power plants.

Useful performance data and operational experience were obtained for the continued development of CCSL's PCCMax technology. A test plan was executed during this period to obtain detailed solvent performance and optimisation data. Importantly, process data was collected to validate



thermodynamic and process models. Thus, the validated CCSL simulation model can be used for the further scale up of the technology.

This article provides a general description of results and operating experiences in the areas of solvent handling, solvent performance, including long term stability testing, energy demand, solvent degradation, corrosion and emissions testing as compared to MEA and the CESAR1 solvent previously tested at Maasvlakte. This was mainly focused on measuring overall regeneration energy, detailed metal content analysis to predict the corrosivity, detailed overall oxidative and thermal degradation, and gas emission characterisation, including aerosols and nitrosamine emissions. Energy consumption of the solvent system per ton of CO₂ captured with a standard flowsheet is around 2.5 GJ per tonne of CO₂. CCSL claim their solvent to be an order of magnitude more stable than MEA for the same application.

14. *Prateek Bumb, Dr Avinash Patkar, P.E, Richard Mather, Ramesh Kumar, Dr. James Hall, Frank Morton and Justin Anthony 'Field Demonstration of Advanced CDRMax Solvent at the USDOE's National Carbon Capture Centre and the CO₂ Technology Centre Mongstad DA, Norway', Carbon Clean Solutions Limited, Southern Company, National Carbon Capture Center (NCCC), 2016*

CCSL have developed the CDRMax solvent for use on power plant flue gases. The solvent has been tested at both the National Carbon Capture Centre, USA, and the Technology Centre Mongstad, Norway. At both centres, the specific reboiler duty, emissions to atmosphere and concentrations of metals in the solvent were measured. The results show that CDRMax was less corrosive and had a lower specific reboiler duty than 30wt% MEA, had low emissions and was resistant to oxidative degradation.

15. *Prateek Bumb, 'Breakthrough CO₂ capture APBS solvent results', Carbon Clean Solutions Limited, 2016*

This PowerPoint file presents the results from the APBS Solvent TCM Campaign in partnership with Imperial College London, UK Department of Energy and Climate Change (DECC), US National Carbon Capture Center and World Economic Forum. The APBS Solvent TCM Campaign was divided into two parts:

- Gas fired CHP campaign (CO₂ inlet concentration 3.6 vol%)
- Cracker gas campaign (CO₂ inlet concentration 13 vol%)

Test campaigns were designed to measure:

- Environmental emissions
- Corrosion
- Energy penalty
- Solvent stability

The presentation states that CCSL successfully demonstrated CO₂ capture of more than 25,000 tonnes CO₂ with no loss of run time due to APBS solvent issues. The APBS solvent was found to be less corrosive than MEA. Therefore, CCSL claim that a cheaper material of construction (\$235) for the cold / rich solvent sides could be used resulting in an overall CAPEX saving of ~ 25%. Aerosol emissions were noted to be 80 times less than for MEA.

2.2.2.2 Costain: Reduced Elevation CO₂ Absorber Programme (RECAP)

16. *Costain website: <http://www.costain.com/media/596752/gas-carbon-capture-oct15-2pp-size-747kb.pdf>*

Costain has designed a novel absorber column to capture CO₂. Its approach involves a novel way of contacting flue gases and the chemical solvent in a cross-flow system. The company claims that this can reduce construction time and cost as well as visual impact. It improves operational



flexibility and potential for upgrading. Costain has developed the basic design with University of Edinburgh, with funding from the UK Department of Energy and Climate Change (DECC).

The University of Edinburgh has continued research into novel cross-flow absorbers. The team tested an elementary packing cell inclined at different angles over a range of gas flow rates to determine the pressure drop, flooding point and onset of flow reversal. The work is due to be published during 2018.

2.2.2.3 Linde / BASF

17. *Krish R. Krishnamurthy, 'Slipstream pilot plant demonstration of an amine-based post-combustion capture technology for CO₂ capture from coal-fired power plant flue gas: DOE funding award DE-FE0007453 2016 NETL CO₂ Capture Technology Meeting', Linde LLC, 2016*

Linde and BASF are partnering in the development of an advanced post-combustion capture technology incorporating BASF's novel amine, OASE® blue, along with Linde's process and engineering innovations. The performance and long term stability was first validated on a 0.45 MWe lignite fired power plant flue gas (Niederaussem, Germany). A nominal 1 MWe pilot plant at the NCCC in Wilsonville, AL, has been commissioned where parametric and long-duration testing was completed to demonstrate stable operation. Functional features were validated during this testing and key performance targets were achieved. The Electric Power Research Institute (EPRI) independent analysis was performed during a long-duration test campaign in June 2016.

The technology was selected by the US Department of Energy (DOE) for Phase 1 of the Large Pilot opportunity. The Phase 2 proposal was submitted with University of Illinois as prime and the Abbott coal fired power plant as host site.

18. *Kevin O'Brien, 'Phase I Results: Large Pilot Scale Testing of Linde/BASF Post-Combustion CO₂ Capture Technology at the Abbott Coal-Fired Power Plant (FE0026588)', University of Illinois, 2016*

These slides are from the Prairie Research Institute (PRI) at the University of Illinois. The university is performing the project management for a project to construct a large pilot scale test of Linde / BASF post-combustion CO₂ Capture technology at the Abbott coal-fired power plant. The aim of the project is to design and install a carbon capture system of nominal 15 MWe integrated with the Abbott Power Plant flue gas system.

Phase I is now completed and the project is planning to move into phase 2, to construct and test a large scale pilot system at the power generator and is currently awaiting award of funding.

2.2.2.4 University of Kentucky

19. *Heather Nikolic, Jesse Thompson and Kunlei Liu, 'Application of a Heat Integrated Post-combustion CO₂ Capture System with Hitachi Advanced Solvent into Existing Coal-Fired Power Plant Award Number DE-FE0007395', University of Kentucky - Center for Applied Energy Research, 2016*

A 2 MWth (0.7 MWe) advanced post-combustion CO₂ capture pilot was tested at Kentucky Utilities E.W. Brown Generating Station. Two solvent testing campaigns (MEA baseline and advanced H3-1) were undertaken. The next step in the technology development pathway is 10 MWe design, fabrication, installation and testing.

20. *Andy Placido, Jesse Thompson, Heather Nikolic, and Kunlei Liu, 'Large Pilot CAER Heat Integrated Post-combustion CO₂ Capture Technology for Reducing the Cost of Electricity Award Number DE-FE0026497', University of Kentucky - Center for Applied Energy Research, 2016*

<https://www.netl.doe.gov/File%20Library/Events/2016/c02%20cap%20review/2-Tuesday/A-Placido-UKCAER-CAER-Heat-Integrated-CO2-Capture.pdf>



These slides give the project overview for the 10MWe advanced post-combustion CO₂ capture pilot including two heat-pump loops, enhanced absorber and water wash design. The host site will be Louisville Gas and Electric Company's Trimble County Generating Station, approximately 80 miles from UKy-CAER. The goal of the project is to develop a pathway to meet the DOE post-combustion CCS targets and bridge the gap to commercialisation by showcasing the unique UKy-CAER process, advancing it from TRL 5/6 to 7/8, and to provide a platform to boost public awareness and confidence in CCS technology. Phase 1 has been completed and the project cost share agreements and host site agreement has been submitted. Phase 2 is pending award of funding.

2.2.2.5 C-Capture

C-Capture is a spin off company from the University of Leeds which aims to introduce new, amine-free solvent materials for CO₂ capture with low cost to ensure commercial viability. It has so far conducted tests at a pre-pilot scale solvent assessment facility in Leeds.

21. *Christopher Mark Rayner, 'Patent: System for the Capture and Release of Acid Gases', C-Capture, US20170001142, 2014*

This patent describes the C-Capture method applied to the capture and subsequent release of CO₂, which 'offers a convenient and simple process which uses inexpensive consumables and offers significant advantages over the methods of the prior art'.

The C-Capture system aims to achieve lower energy requirements for CO₂ capture and to operate at much lower temperatures (preferably ambient temperature), while minimising atmospheric emissions and degradation, thus improving on the traditional solvent CO₂ capture process. The main steps of the process are laid out in the patent as follows:

- 1) Capturing at least one acid gas by contact with a capture composition comprising at least one salt of a carboxylic acid and at least one water-miscible non-aqueous solvent.
- 2) Releasing that acid gas by adding at least one protic solvent or agent to said composition.
- 3) Regenerating the capture composition by partial or complete removal of said added protic solvent or agent from said composition.

22. *'DECC Energy Entrepreneurs Fund Phase 4 Supported Companies', Department of Energy and Climate Change, 2014*

C-Capture Ltd (C-CL) from Leeds University had created a family of amine-free post-combustion capture solvents that were thought to match the steam requirements of the best second-generation amine solvents but also with significantly reduced toxicity, environmental impact and corrosion characteristics. In this project, variants of C-CL's amine-free chemistry were screened for suitability in the laboratory and scaled-up on the company's dedicated pre-pilot test rig in order to identify optimum candidates. These were then tested on post-combustion capture simulation rigs to confirm their superiority to second-generation amine solvents. The results were planned to have been used in licensing negotiations with manufacturers of CCS plant and chemicals.

23. *<http://www.carboncapturejournal.com/news/c-capture-receives-150000-as-shell-springboard-national-winner/3730.aspx?Category=all>, 2016*

C-Capture received £150,000 as the Shell Springboard National Winner for its innovation which removes CO₂ from industrial gas streams. Shell Springboard is one of two Enterprise Development programmes run by Shell to support and inspire UK entrepreneurs to innovate for a lower-carbon future.

2.2.3 Encapsulated Solvents

While some interesting lab-scale progress has been made since the publication of the IEAGHG 2014 report, it does not appear that the technology has advanced more than one or two levels. Wood judges that this technology may now be at TRL-2 to 3.



24. *IEAGHG 'Assessment of Emerging CO₂ Capture Technologies and their Potential to Reduce Costs', December 2014*

The IEAGHG 2014 paper describes the encapsulated solvent technology as a new concept in which the operating fluid, amines or carbonates are enclosed in a thick polymer shell forming 220-400 µm beads. The beads are intended to dramatically increase the surface area of the solvent in contact with the flue gas, which the paper likens to how the alveoli act in mammalian lungs. The report names one technology provider: a team from the University of Illinois Urbana-Champaign, Babcock and Wilcox, and Lawrence Livermore National Laboratory. According to the report, their first experiments on encapsulated solvents have indicated some potential but that it is too early to formulate a full application until more has been done to characterise and optimise capsule performance. Therefore, the IEAGHG had assessed the technology to be TRL-1.

25. *Lawrence Livermore National Laboratory 'Encapsulated liquid sorbents for carbon dioxide capture', Feb 2015*

This article by the technology provider team referenced in the IEAGHG 2014 report is on microencapsulation of solvents in polymer microcapsules composed of liquid carbonate cores and highly permeable silicone shells which are produced by microfluidic assembly. The article describes their new class of sorbent materials that have been created to combine the advantages of liquid solvents (that is, high capacity, high selectivity and water tolerance) and solid sorbents (for example, high surface area and low volatility). The article claims that they have created a highly permeable, microencapsulated carbon sorbent. The inner fluid is composed of an aqueous potassium or sodium carbonate solution with or without a pH indicator dye and catalyst for enhanced CO₂ absorption. The middle fluid, the capsule shell, is a photopolymerisable silicone, and the outer fluid, the carrier, is composed of an aqueous solution with stabiliser and surfactant.

The measured CO₂ permeability of the shell material is 3,260 barrer, which the article claims is quite high compared with most gas separation membranes and comparable to values reported for other silicones.

26. *Lawrence Livermore National Laboratory 'Microencapsulation of Advanced Solvents for Carbon Capture', April 2016*

This paper discusses the research to identify a viable technique to encapsulate solvents including ionic liquids and CO₂-binding organic liquids for efficient use in carbon capture systems. Lawrence Livermore National Laboratory claim to have developed two polymer formulations that show promise as shell materials for a range of ionic liquids and CO₂-binding organic liquids. They have made the first demonstration of an encapsulated ionic liquid for carbon capture, and shown that encapsulation enhanced the rate of CO₂ absorption. However, the paper concedes that the current formulation of SiTRIS/ NDIL0231 does not quite meet the required criteria as a good match for shell material and solvent. Lawrence Livermore conclude that "Our past experience with encapsulation suggests there are many remaining avenues to explore and further improvement in encapsulated advanced solvents is likely."

27. *Joshuah K. Stolaroff, 'Advanced Manufacturing To Enable New Solvents and Processes For Carbon Capture: NETL CO₂ Capture Technology Meeting', Lawrence Livermore National Laboratory, 2016*

This reference includes an interesting graph, on slide 7, on the additional surface area that can be formed by permeable solids. Printed composites and microcapsules are the areas where Lawrence Livermore is focusing its research. On the graph, these two technologies are shown to have the greatest interfacial area per reactor volume.

2.2.4 Precipitating Solvents

Wood judge that the chilled ammonia process may now be at TRL-6. However, since it is no longer operating as a precipitating solvent, this cannot be considered to improve the TRL of precipitating solvents. Therefore, the TRL for precipitating solvents remains at 5-6 as stated by the IEAGHG, assuming that other parties are still investigating them with the precipitation element.



28. *IEAGHG 'Assessment of Emerging CO₂ Capture Technologies and their Potential to Reduce Costs', December 2014*

For precipitating solvent technology, solvents such as potassium carbonate and amino acid salts precipitate out of solution when reacted with CO₂. The precipitating solvent allows a lower energy requirement for solvent regeneration and makes it possible to regenerate the precipitated solvent at a higher pressure, which can result in energy savings from CO₂ compression. The paper states that activated potassium carbonate is the most mature technology for precipitating solvents. The IEAGHG report gives the technology a TRL-4 to 5.

The report states that it is not clear to what extent all of the systems needed to handle solids have been proven in an integrated system for precipitation solvents. For example, Alstom have developed the chilled ammonia process (CAP) with precipitation but they are currently operating their pilot plants without precipitation.

2.2.4.1 General Electric

29. *J. Perry, Teresa A. Grocela-Rocha, Michael J. O'Brien, Sarah Genovese, Benjamin R. Wood, Larry N. Lewis, Hubert Lam, Grigori Soloveichik, Malgorzata Rubinsztajn, Sergei Kniajanski, Sam Draper, Robert M. Enick, J. Karl Johnson, Hong-bin Xie and Deepak Tapriyal 'Aminosilicone Solvents for CO₂ Capture', GE Global Research, GE Energy, Department of Chemical and Petroleum Engineering University of Pittsburgh, 2010*

This paper describes a study on the use of an aminosilicone solvent mix for the capture of CO₂. To maintain a liquid state, a hydroxyether co-solvent was employed which allowed enhanced physisorption of CO₂ in the solvent mixture. Regeneration of the solvent system was demonstrated over six cycles and the absorption isotherms observed indicate a 25–50% increase in CO₂ capacity over 30% MEA. In addition to this finding, a proof-of-concept for continuous CO₂ absorption was demonstrated. Additionally, modelling to predict heats of reaction of aminosilicone solvents with CO₂ was in good agreement with experimental results. Further exploration of this system is reported to be in progress with thermal stability and corrosivity studies underway as well as further optimisation of the aminosilicone substrate. Finally, a laboratory-scale continuous absorption and desorption unit is under construction, which will provide the kinetic data needed for further development.

30. *Michael Matuszewski 'Bench-Scale Process for Low-Cost Carbon Dioxide (CO₂) Capture Using a Phase Changing Absorbent', National Energy Technology Laboratory, 2014*

This paper from 2014 lays out the plan for the General Electric Global Research (GEGR) novel bench-scale test of their aminosilicone-based phase-change process for post-combustion CO₂ capture. GEGR planned to utilise the phase-changing solvent (GAP-0) tested under a previous Advanced Research Projects Agency-Energy (ARPA-E) funded project. The GAP-0 solvent was proven to readily form a solid in the presence of CO₂ in a thermally reversible reaction with no apparent degradation of the absorbent.

The process disperses the liquid absorbent into the absorber as fine droplets for rapid reaction with CO₂ to form a dry, conveyable solid. Bench-scale testing and analysis of an improved version of this novel process were intended to show its feasibility and scalability. In this project, a phase-changing solvent-based, bench-scale CO₂ capture system was to be constructed, integrating an absorber unit, a solids transfer operation, and a CO₂ desorber into a continuous system. It was also to include recycle of the absorbent through all of the unit operations.

Project objectives were to generate preliminary process and cost models; design and build a bench-scale system; perform bench scale testing on unit operations; perform an environmental, health and safety (EH&S) risk assessment; perform continuous bench-scale system testing; and complete techno-economic and scale-up analyses. This work was due to be completed in 2016.



31. *'Improvement of GE Power's Chilled Ammonia Process using Membrane Technology Large Pilot Scale Post Combustion CO₂ Capture No. FE0026589 National Energy Technology Laboratory Department of Energy', General Electric Company, 2016*

The project considered the use of liquid-liquid membrane technology to improve General Electric's Chilled Ammonia Process (CAP) CO₂ capture technology. The slides state that the decision was made not to proceed with the Large Pilot Modifications and application for Phase II funding.

32. *'CO₂ Capture Large-scale Pilot Test: FE0026498 Presentation at CO₂ Capture Meeting FE0026589 National Energy Technology Laboratory Department of Energy', General Electric Company, 2016*

These slides present the General Electric (GE) large pilot-scale CO₂ capture project using their aminosilicone solvent. The first objective of the project was to achieve 10 MW scale with sustained 90% capture and performance consistent with \$40/mtCO₂ capture cost over two months of continuous operation. The second objective was to demonstrate a low solvent loss rate and establish diversity of solvent supply.

The slides state that because of the delay in the pilot test at NCCC, GE could not support a TRL-6 claim in March 2016 and declined to submit a Phase 2 renewal application. The plan is to resume work on the Phase 1 deliverables in October or when GE have a vetted data set from the NCCC test. GE aimed to complete the deliverables by March 2017.

33. *Ola Augustsson, Barath Baburao, Sanjay Dube, Steve Bedell, Peter Strunz, Michael Balfe, Olaf Stallmann, '13th International Conference on Greenhouse Gas Control Technologies, GHGT-13, 14-18, November 2016, Lausanne, Switzerland: Chilled Ammonia Process Scale-up and Lessons Learned', General Electric Company, 2017*

This work summarises the bench-scale, pilot-scale, and validation facility results and offers insights into the lessons learned and effort required bringing the technology to commercialisation at an industrial scale.

The technology was successfully tested on flue gases produced from coal, oil, and natural gas combustion and flue gas produced from refinery applications. Operational experience and data validation of lab-scale tests was fed back into refinement of the process design. The tests indicated that further improvements are possible and it is stated that the process is ready for demonstration scale projects. However, it is noted that the system operates better when designed not to precipitate solids.

2.2.5 Biphasic Solvents

Since the most developed process, the IFP DMX process, did not progress to the planned industrial plant pilot test at Brindisi, and no other pilot references have been identified during the course of this study, there does not appear to have been any TRL progress since the IEAGHG 2014 report. Therefore, Wood judge this technology to currently remain at TRL-4.

34. *IEAGHG 'Assessment of Emerging CO₂ Capture Technologies and their Potential to Reduce Costs', December 2014*

The term "biphasic solvent" refers to solvent processes in which two liquid phases are formed once CO₂ is absorbed in the solvent. The heavy liquid phase contains the CO₂ and this liquid phase is separated out by gravity and sent for CO₂ regeneration. This reduces the regeneration energy requirement. The IEAGHG report states that several groups are investigating two-phase liquid solvents. The University of Dortmund, Germany, have been developing their 'Thermomorphic Biphasic Solvent' for several years. The IFP 'DMX' solvent concept was also being tested at a pilot plant with future activities planned to test the solvent under real process conditions as part of the OCTAVIUS project. The IFP DMX-1 process was under evaluation to be tested at Enel's Brindisi pilot plant, Italy. However, it seems that this large scale demonstration has now been cancelled.



35. *Ludovic Raynal, Patrick Briot, Matthieu Dreillard, Paul Broutin, Angela Mangiaracina, Benedetta Salghetti Drioli, Monia Politi, Cristiana La Marca, Jan Mertens, Marie-Laure Thielens, Géraldine Laborie and Laurent Normand "Evaluation of the DMX Process for Industrial Pilot Demonstration – Methodology and Results", IFP Energies Nouvelles, Enel Ingegneria e Ricerca SpA, Laborelec, Prosernat, 2014*

The IFP DMX process is described in more detail in this paper. It is based on the particular property of demixing solvents which form two immiscible liquid phases when CO₂ is absorbed. The light phase is almost free of CO₂, only the high capacity heavy phase is sent to the stripper. This makes energy savings possible but also requires an adapted process flow scheme and extra equipment. Most of this paper deals with the evaluation of the process benchmarked against MEA, and the acceptable cost for the retrofit of the existing industrial pilot.

The paper has a detailed process flow scheme for the DMX process. In order to get a meaningful comparison between DMX and MEA processes, a heat integration study between the power plant and the capture unit has been jointly performed by ENEL and IFPEN. For both processes, the same steam cycle scheme has been selected. However, for each process, turbine pressures have been adjusted while maintaining constant electrical power output to obtain an appropriate steam pressure for extraction to the CO₂ capture unit.

The information in the report is sparse with regard to costs and there is no heat and material balance. A first comparison of performance between MEA and DMX shows that the DMX process has 22% lower energy consumption than the MEA process, when both CO₂ removal and compression systems are accounted for.

The DMX solvent is also highlighted in the IEAGHG 2014 report as being one of the most developed two-phase liquid solvent technologies; it is one of very few novel physical solvent technologies that has been tested at industrial pilot plant scale. The SP3 subproject of the OCTAVIUS EU FP7 project was dedicated to the demonstration of the DMX CO₂ capture process on the 3.5 MWe equivalent industrial pilot of ENEL at Brindisi, but as mentioned above, this stage was cancelled.

36. *Paul Feron, 'Absorption-Based Post-Combustion Capture of Carbon Dioxide', Woodhead Publishing, 2016*

This book has a chapter on the DMX system of IFP Energies Nouvelles, which summarises the DMX process presented by Raynal in 2014.

37. *Diego D.D. Pinto, Hanna Knuutilaa, Georgios Fytianos, Geir Haugen, Thor Mejdell, Hallvard F. Svendsen "CO₂ Post Combustion Capture with a Phase Change Solvent. Pilot Plant Campaign", Department of Chemical Engineering, SINTEF Materials and Chemistry, 2014*

This paper is on the 5 molar tertiary amine (DEEA) and 2 molar diamide (MAPA) mixture which was tested in the Gløshaugen (NTNU / SINTEF) pilot plant. The phase change solvent showed to operate well in the pilot plant. Neither high viscosity nor foaming issues were noted. Absorption was reasonably fast and the CO₂ stripping in this system was easy due to the presence of a tertiary amine. The system was able to operate at significantly lower specific reboiler duty and reboiler temperatures compared to the benchmark 30 wt% MEA. The solvent was, however, more volatile than MEA and better control is required to avoid solvent losses.

38. *Diego D.D. Pinto, Syed A.H. Zaidy, Ardi Hartono, Hallvard F. Svendsen 'Evaluation of a Phase Change Solvent for CO₂ Capture: Absorption and Desorption Tests', Department of Chemical Engineering, Norwegian University of Science and Technology, 2014*

This report describes a lab scale study where a blend of a tertiary amine (DEEA) and a diamine (MAPA) was studied in the screening apparatus for preliminary absorption tests. Two immiscible liquid phases were formed once the CO₂ was absorbed and the system was shown to have a large capacity for CO₂. The two phases were analysed individually for both amines and CO₂. MAPA and



water were found concentrated in the heavy CO₂ rich phase whereas the CO₂ lean phase consisted mainly of DEEA.

The CO₂ rich phase was heated to desorption temperatures and shown to regenerate CO₂ at higher pressures than normally used for 30 wt% MEA. The data enabled understanding of the system behaviour and showed that the system has potential for significant reduction in regeneration heat through high cyclic capacity, high CO₂ stripping pressures, and for operating where the heat of reaction lies between primary and tertiary amines. The tests also give good estimates for the absorption rate at higher loadings. The data generated in this experiment are of great value for further modelling purposes. None the less, more experiments need to be carried out to confirm the system's potential as a solvent for CO₂ capture.

39. *Ludovic Raynal, Cristina La Marca, Jan Mertens, Laurent Normand and Paul Broutin 'Demonstration of the DMX Process Description of the Octavius SP3 Project', IFPEN, ENE, Laborelec, Prosernat, 2013*
40. *Zhiwu (Henry) Lianga, Wichitpan Rongwong, Helei Liua, Kaiyun Fu, Hongxia Gao, Fan Cao, Rui Zhang, Teerawat Sema, Amr Henni, Kazi Sumon, Devjyoti Nath, Don Gelowitz, Wayuta Srisang, Chintana Saiwan, Abdelbaki Benamor, Mohammed Al-Marri, Huancong Shi, Teeradet Supap, Christine Chan, Qing Zhou, Mohammad Abu-Zahra, Malcolm Wilson, Wilfred Olson, Raphael Idem, Paitoon (PT) Tontiwachwuthikul 'Recent Progress and New Developments in Post-Combustion Carbon-Capture Technology with Amine Based Solvents', Joint International Center for CO₂ Capture and Storage (iCCS), Energy Informatics Laboratory, Petroleum and Petrochemical College, Gas Processing Center, Institute Centre of Energy (iEnergy), International Test Centre for CO₂ Capture (ITC), 2015*
41. *P. Broutin^{1*}, P. Briot, S Ehlers, A Kather 'Benchmarking of the DMXTM CO₂ Capture Process', IFP Energies Nouvelles, TUHH, 2013*
42. <https://az659834.vo.msecnd.net/eventsairwesteuprod/production-ieaghg-public/6e92e3c3b0ff457fbf9ac7123c83bbe1>

These papers have been reviewed. However, they did not contain any further information additional to the sources described above.

2.2.6 Ionic Liquids

Ionic liquids are non-volatile salts that form a liquid phase at ambient or slightly elevated temperatures. They are considered as a potential solvent for post-combustion CO₂ capture since they have low vapour pressures resulting in low losses and reduced environmental impact, when compared to conventional amine-based solvents.

From a commercial perspective, the IEAGHG gave ionic liquids a TRL-1. The IEAGHG summarise that ionic liquids may struggle to compete with conventional absorption systems because their absorption capacity is likely to be much lower, which may explain why ION engineering appear to have moved away from a pure ionic liquid approach, preferring a blend of amines and other constituents. Wood concludes that this technology remains at TRL-1.

43. *IEAGHG 'Assessment of Emerging CO₂ Capture Technologies and their Potential to Reduce Costs', December 2014*

The IEAGHG report describes ionic liquids as suitable for CO₂ absorption due to their high physical and chemical CO₂ solubility, with high stability and negligible vapour pressure. The ionic liquids used in CO₂ absorption are inorganic or organic salts, which are considered safer alternatives compared to volatile organic solvents, due to their non-volatile nature at ambient conditions. The IEAGHG report names a number of groups that are developing the technology. The University of Notre Dame, Imperial College London and a number of universities in China have been focusing on improving ionic liquids. Georgia Tech Research Corporation has been developing reversible ionic liquids and Du Pont is looking at CO₂ solubility and phase behaviour for different ionic liquids.



2.2.6.1 ION Engineering

44. Erik Meuleman, 'ION Advanced Solvent CO₂ Capture Pilot Project DE-FE0013303 NETL 2016 CO₂ Capture Technology Conference', ION Engineering, 2016

ION Engineering has developed proprietary ionic liquid for CO₂ capture with partners and contractors such as The University of Alabama, Worley Parsons, Energy and Environmental Research Centre (EERC), EPRI, Excel Energy, Evonik and Elstron R&D. A pilot plant at ION Engineering was in use and a 0.2 MW test at the EERC in North Dakota started in 2012.

The slides present a 45-month project running from Oct 2013 to June 2017 entitled 'ION Advanced Solvent CO₂ Capture Pilot Project'. The project involves a 0.6 MWe test campaign at the National Carbon Capture Center (NCCC) and a 12 MWe test campaign at the Technology Centre Mongstad (TCM). The total project funding is \$25.2M, of which \$16.4M comes from the DOE and the remainder \$8.9M is provided by ION and Partners.

The ION CO₂ Capture system is designed to achieve 90% capture and produce a CO₂ product purity of ≥ 99% at 153 bara. The ION 2016 techno-economic assessment was performed by Sargent & Lundy using ION's ProTreat® simulations, whose model was validated by the NCCC test campaign. The performance results showed a 38% incremental reduction in CAPEX, 28% incremental reduction in OPEX, 32% decrease in ICOE and a cost of capture of between \$39-\$45 per tonne of CO₂. However, it is noted that at some point during the development of their technology, ION Engineering have moved away from their ionic liquid and instead now use a more conventional solvent.

2.2.7 Enzyme Catalysed Absorption

Since CO₂ Solutions have an operating 10 TPD field demonstration plant of their technology, Wood concludes that the enzyme catalysed absorption process has reached TRL-6.

45. IEAGHG 'Assessment of Emerging CO₂ Capture Technologies and their Potential to Reduce Costs', December 2014

Enzymes can be used to catalyse the CO₂ absorption process in carbonate / bicarbonate (potassium carbonate) solvents. The pure carbonate / bicarbonate has limitations on the CO₂ absorption rate. Enzymes have the potential to be used as an activator to accelerate the CO₂ absorption rate. In this process, the enzymes are clustered together in a cross-linked enzyme aggregate (CLEA) and filtration is used to separate the enzyme from the CO₂ rich solvent before the solvent is sent for CO₂ regeneration.

The IEAGHG report presents that currently CO₂ Solutions (Canada), Novozymes and Carbozymes are developing their proprietary enzymes for CO₂ absorption processes, with the technology still being at proof of concept level. The IEAGHG has therefore assessed that the technology readiness level is TRL-1.

46. CO₂ Solutions Website: <http://www.co2solutions.com/>

In 2012 and 2013, CO₂ Solutions secured \$5.2M in grant funding from the Government of Canada's ecoENERGY Innovation Initiative and the Alberta Government's Climate Change and Emissions Management Corporation (CCEMC) towards a \$7.5 million project to optimise and pilot the technology for CO₂ capture from oil sands production.

In 2014, CO₂ Solutions completed the internal development of a new high-performance enzyme which demonstrated longevity and catalytic performance significantly surpassing that of the best third-party enzymes used by the Corporation to date. Subsequently, CO₂ Solutions tested its technology at the University of North Dakota Energy & Environmental Research Center (EERC) at initial pilot scale using natural gas and coal flue gas. The results showed strong potential to provide for a cost of CO₂ capture of less than US\$40 per metric tonne, significantly below the cost of conventional technology while generating no waste products.



In May 2015, CO₂ Solutions completed the construction of its larger 10 tonne-CO₂/day capture field demonstration unit. Operating in Salaberry-de-Valleyfield, Quebec, a total of 2500 hours of testing operations is planned which is expected to confirm the favourable economics and environmental friendliness of the process for commercial power and steam plant application.

In June 2015, the Corporation entered into a collaboration agreement with GasTran Systems (GTS), a leading provider of high-intensity gas-liquid rotating packed bed (RPB) mass transfer technology to bring to market an advanced carbon capture solution.

47. *L. Fradette et al., 'CO₂ Solutions Demonstration Results of Enzyme-Accelerated CO₂ Capture', GHGT-13, November 2016.*

These slides from the CO₂ Solutions presentation at GHGT-13 document its progress from lab-scale testing prior to 2014, through its 1 TPD pilot from 2014 to 2015 and its 10 TPD demonstration in 2015. Some findings from the pilot's operation are documented and plans for future scale up, but it is not clear from the slides if there is a timescale and firm plan for a larger plant.

2.2.8 Algae Based Capture

The technology was given a TRL-1 by the IEAGHG for large power plants in 2014. Since some limited tests have subsequently been performed in a controlled environment, Wood assesses that the technology readiness level has increased to TRL-3. However, challenges regarding the large volume of algae required for a commercial power plant still exist.

48. *IEAGHG 'Assessment of Emerging CO₂ Capture Technologies and their Potential to Reduce Costs', December 2014*

The photosynthesis reaction involves reacting light energy, water and CO₂ to form oxygen and simple sugars. In most plant species, photosynthesis is an inefficient reaction with slow kinetics: this is especially true for larger plant species. However, for simpler and smaller plants, the efficiency of the photosynthesis reaction (light energy to chemical energy) is comparatively high, as they do not need to invest as much energy in building large structures. Single cell algae are the smallest and simplest form of plant, and thus can commit all of their energy to reproduction. In this process, a photo-bioreactor is used to optimise the photosynthesis process by adjusting the conditions of light, pH, CO₂ and nutrients. A pump is used to make the cultures re-circulate within the tube and the CO₂ is pumped into the tubes by air pumps. The photo-bioreactor can be used for the outdoor mass cultures due to the large illumination surface.

Eni Technology have conducted a field experiment of CO₂ uptake by algae in a raceway pond. The CO₂ supplied was from natural gas turbine flue gas. Green Fuel is investigating photo bioreactors which bubble flue gas through high-rate micro-algae for CO₂ and NO_x removal. Idaho National Lab are investigating the uptake of inorganic carbon in a photosynthesis reactor with bacteria, which raises the pH and promotes calcium carbonate precipitation. Duke Energy and partners have a project at Easy Power Plant in Kentucky to demonstrate an algae based system for CO₂ mitigation from coal fired power plants.

The IEAGHG report concedes that it is questionable if work on micro-algae should be included in the scan of capture technologies. There are large questions around the application of the technology to commercial scale fossil fuel power plants. To capture 90% of the emissions from a coal power plant producing 10,000 tonnes per day of CO₂, an area of 625 km² would be required.

49. *Jim Lane, 'PHYCO2, MSU "breakthrough" grows algae 24/7 without sunlight', Biofuels Digest, March 2016*
<http://www.biofuelsdigest.com/bdigest/2016/03/20/phyco2-msu-breakthrough-grows-algae-247-without-sunlight/>

This online reports outlines work performed by PHYCO2 and Michigan State University on a small stream of flue gas from the university's T.B. Simon Power Plant. The trials have focused on demonstrating that algae can be grown in a high-density enclosed environment, rather than in open ponds. PHYCO2 claims that their patented HILED Algae Photo-bioreactor can generate algae



yields up to six times those possible in an open environment. Extrapolating from the IEAGHG conclusions above, an area of approximately 100 km² would be needed to capture 90% of the CO₂ emissions from a coal power plant producing 10,000 tonnes per day of CO₂.

2.3 Membranes

2.3.1 Polymeric Membranes

A lot of development work has gone into improvements in membranes for post-combustion CO₂ capture. However, much of the most significant work was already underway at the time of the IEAGHG 2014 report, and it is not clear from more recent literature whether a fully functioning prototype has been developed. It is possible that MTR now have one, and others are known to be pursuing this technology. However, no public domain references could be found to support an increase in the TRL for either polymeric membranes in isolation or their combination with low temperature separation processes. Wood therefore concludes that polymeric membranes and membrane / cryogenic hybrid system technologies remain at TRL-6.

50. *IEAGHG 'Assessment of Emerging CO₂ Capture Technologies and their Potential to Reduce Costs', December 2014*

The report focuses on three types of membranes: polymeric membranes, hybrid membranes and polymeric membranes with low temperature separation. The report references the NETL 2012 report for the majority of the cost requirement / cost evaluation for polymeric membranes.

There are several groups developing membrane technology for post combustion carbon capture. The EU project nanoGOWA has tested a diffusion transport membrane and a fixed site carrier membrane at a power plant in Germany. The NTNU-patented polyvinylamine (PVAm) membrane together with fixed amine groups (which act as a carrier for CO₂), is evaluated at a pilot plant at an EDP power plant in Portugal. The PVAm+FCS membrane test results are promising for extremely high separation of CO₂ at a low feed pressure.

Membrane Technology Research Inc. (MTR) was testing its membrane Polaris in a 1 MW unit at DOE's National Carbon Capture Center (NCCC) in Wilsonville, Alabama from 2013. Other organisations such as MEMFO, NTNU, and SINTEF Norway; Membrane Technology Group and Twente University; Center of Membrane Technology Group and NJIT; and RTI International are active in the area of membrane based CO₂ separation process development.

Due to several pilot plant tests at a large scale and the deployment of membranes in other applications the IEAGHG have assessed that development of membranes for commercial use could be achieved relatively quickly. It has therefore assigned membranes a technology readiness level of TRL-6.

51. *Visakh P. M., Olga Nazarenko 'Nanostructured Polymer Membranes, Volume 2: Applications' John Wiley & Sons, 26 Aug 2016*

This book discusses the applications of polymeric membranes for removing CO₂ from flue gas. The book highlights the challenges involved in membrane separation due to the low concentrations of CO₂ present in the large volumes of flue gas, along with the high purity required. The only technology provider mentioned in the book for CO₂ capture is the MTR Polaris membrane.

52. *Jonathan Forsyth, Stuart Lodge, Stefano Consonni, Daniele Di Bona, Manuele Gatti, Emanuele Martelli, Roberto Scaccabarozzi, Federico Viganò 'Evaluation of five alternative CO₂ capture technologies with insights to inform further development: 13th International Conference on Greenhouse Gas Control Technologies, GHGT-13, 14-18 November 2016, Lausanne, Switzerland', BP International Limited, Consorzio LEAP – Laboratorio Energia e Ambiente Piacenza, November 2016*

This report evaluated five different alternative CO₂ capture technologies for the 13th International Conference on Greenhouse Gas Control Technologies, specifically focusing on post-combustion



CO₂ capture from natural gas derived exhaust gases. The report used the scheme described by Merkel et al for the polymeric membrane technology, resulting in a calculated LHV efficiency of 48% and a total specific plant cost of \$ 2,332 / kW (2014 basis). The paper concludes that the membrane material needs improvement, particularly in terms of permeability, to allow CO₂ capture with lower mechanical energy penalty and lower membrane area. The membrane module cost used in the capital cost estimation in the report is much lower than the current cost and is based upon future mass production of the material and module packaging. The operating costs used assume that the membrane material is durable and capable of long service life. The analysis suggests that the minimum avoided cost for this technology may be found at a substantially lower capture rate than the 90% typically targeted. It concludes that the technology could be particularly suited to smaller scale applications where solvent systems may be less cost-effective.

53. *Lora Toy, Atish Kataria, Raghubir P. Gupta 'CO₂ Capture Membrane Process for Power Plant Flue Gas Final Technical Report' RTI International, April 2012*

This article states that RTI international, in collaboration with Arkema, Inc. and Generon IGS, Inc., have developed an advanced, hollow-fibre, polymeric membrane process that could be retrofitted into current coal-fired power plants to capture at least 90% of the CO₂ from plant flue gas with 95% captured CO₂ purity.

54. *Paul Glaser, Fred Stewart, Bill Koros 'Composite Hollow Fiber Membranes for Post Combustion CO₂ Capture Project Close Meeting', 2013*

This paper describes a project to develop bench-scale coated composite hollow-fibre membrane materials and processes for CO₂ / N₂ separation in coal flue-gas with at least 90% CO₂ capture and less than 35% increase in levelised cost of electricity. Polyphosphazene materials were used in a selective layer in combination with a Torlon (polyamide-imide) porous support. Significant difficulties involving performance degradation, both in permeance and in selectivity over time were identified and partially addressed using a variety of techniques, but significant barriers to implementing candidate materials in a robust system remained at the end of the award period. Alternate routes towards increasingly more robust systems and lines of further inquiry were identified for subsequent work.

2.3.2 Polymeric Membranes / Cryogenic Separation Hybrid

55. *IEAGHG 'Assessment of Emerging CO₂ Capture Technologies and their Potential to Reduce Costs', December 2014*

The report highlights the improved performance potential of polymeric membranes with low temperature separation and other hybrid membrane systems.

Air Liquide has run a bench scale test for the membrane in operation at -25 to -45°C. Linde Engineering is also involved in developing low temperature CO₂ purification technology.

IEAGHG has given this technology a TRL-6, as the majority of components in this process are at a similar development stage to that of the full membrane process but membrane performance requirements will be more relaxed. The CO₂ liquefaction element can be based in well-developed cryogenic processes such as Liquefied Natural Gas (LNG) production.

56. *Timothy C. Merkel, Xiaotong Wei, Zhenjie He, Lloyd S. White, J. G. Wijmans, and Richard W. Baker "Selective Exhaust Gas Recycle with Membranes for CO₂ Capture from Natural Gas Combined Cycle Power Plants", Membrane Technology & Research, Inc., 2012*

This report applies the MTR polymeric membrane technology to natural gas combined cycle power plant. This paper includes an exhaust gas recycle (EGR) element developed to address the low CO₂ content in NGCC flue gas. In this process, a portion of the flue gas is recycled to the inlet of the air compressor and replaces some of the air going to the combustor. Because natural gas turbines operate with a large excess of air (~250%), EGR can increase the flue gas CO₂ content without adversely impacting the combustion turbine performance. The paper describes a membrane process that allows CO₂ to be selectively recycled in an NGCC power system. By using



combustion air as a sweep stream, CO₂ can be stripped from flue gas, selectively recycled, and pre-concentrated with little energy input. Subsequent capture of the CO₂ from a concentrated stream requires less energy than capture from the original dilute flue gas and can be accomplished with membranes.

Figure 4 in the paper shows the difference between the concentration of CO₂ and oxygen in the flue gas for selective recycle and conventional recycle. Because the membrane selectively recycles CO₂, the flue gas enrichment is achieved without significantly diluting oxygen in the combustion air stream. For example, with 19% CO₂ in the flue gas, the oxygen content in the combustion air stream is 16% when selective recycle is used. At a similar oxygen concentration, conventional EGR produces a flue gas stream containing only 6.5% CO₂.

The paper also looks at the minimum energy of separation of CO₂ from the flue gas. The results show that the selective recycle process has a lower minimum energy of separation per tonne of CO₂ captured as a function of the CO₂ capture rate than conventional processes. The thermodynamic minimum energy is obtained by calculating the difference between the Gibbs Free Energy of the initial stream to be separated and the Gibbs Free Energy of the streams produced after separation, compression, and liquefaction. The report used the process simulator ChemCad 6.3 to obtain the Gibbs Free Energy values of the streams, thereby utilising the thermodynamic database (Soave–Redlich–Kwong) incorporated in the simulator.

The report uses the same membrane process design as used in the NETL 2012 report for coal fired power plants (see below), and thus the IEAGHG 2014 report. The primary difference from the coal case is that a greater CO₂ enrichment factor is possible with natural gas. For example, while coal flue gas can be enriched from 12% to ~20% using a series-selective recycle membrane step, the same membrane configuration can enrich natural gas flue gas from 4% to 22%. This enhanced enrichment is possible because natural gas combustion uses more excess air than coal combustion (200%–250% versus 10%–15%); therefore, there is more flexibility to recycle CO₂ with a sweep membrane in the NGCC case without approaching stoichiometric oxygen limits.

57. NETL 'Current and Future Technologies for Power Generation with Post Combustion Carbon Capture Final Report', 2012

The MTR design studied in this report was for a coal fired power plant. It assumes the successful development and the achievement of high performance levels beyond what is possible with current membrane technology.

The total MTR membrane surface area needed with the selected distribution of cross-flow and counterflow membranes in the process is estimated to be 1,500,000 m² using simplified, numerical models for the spiral-wound membrane vessels.

The model indicates the sensitivity of the total membrane surface area needed to the distribution of the plant CO₂ removal between the cross-flow and counter-flow membranes. Without using the counter-flow membrane, this process would require a very large cross-flow membrane with very high capital investment. Each membrane should remove CO₂ at nearly equal rates to achieve a low total membrane surface area, and consequently the counter-flow, air sweep membrane needs to achieve about 90% removal of CO₂ from its inlet stream. The large recycle of CO₂ to the boiler increases the CO₂ content of the flue gas to the cross-flow membrane greatly, achieving about 21 mol% CO₂.

58. Colin A. Scholes, Minh T. Ho 2 and Dianne E. Wiley "Membrane-Cryogenic Post-Combustion Carbon Capture of Flue Gases from NGCC", Department of Chemical and Biomolecular Engineering, The University of Melbourne & School of Chemical Engineering, University of New South Wales, 2016

The paper models the Merkel et al scheme in HYSYS. The paper concludes that the three CO₂-selective membrane with liquefaction and O₂-enrichment process is not shown to be competitive for post-combustion carbon capture compared to conventional chemical absorption technology when applied to the flue gas of a NGCC. The process achieved a minimum in cost of capture when a significant amount of CO₂ was recycled through the turbine in the combustion air. The feed blower



accounts for almost half of the energy duty of the plant, due to the high gas throughput. This highlighted the strong dependence the membrane-liquefaction process design has on CO₂ partial pressure in the flue gas to be competitive with other CO₂ separation technologies.

59. *T. Chaubey, S. Kulkarni, A. Augustine, D. Hasse, J. Brumback, D. Kratzer, D. Calvetti, J. Ma 'CO₂ Capture by Cold Membrane Operation with Actual Power Plant Flue Gas' NETL CO₂ Capture Technology Meeting 2015, Air Liquide, June 2013*

This presentation covers the Air Liquide current project to test their cold membrane technology at 0.3 MWe scale (TRL5) at the National Carbon Capture Center (NCCC). The total budget for the project was \$5.88MM, of which the DOE funded \$4.7MM. The project was due to finish at the end of 2016.

2.3.3 Room Temperature Ionic Liquid (RTIL) Membranes

60. *IEAGHG 'Assessment of Emerging CO₂ Capture Technologies and their Potential to Reduce Costs', December 2014*

Room Temperature Ionic Liquids can be formed into gels to become "Gel-RTILs" by incorporation with low molecular weight organic gelators (LMOGs). Gelation is a thermo-reversible process with transition temperatures ranging from 20 to 180°C which allows the material to be formed into membranes. This membrane has demonstrated high perm-selectivity for CO₂ over other components of coal-fired power plant exhaust gas. Gel-RTILs maintain CO₂ affinity and permeability characteristics of RTILs. A low fraction of LMOG is required, typically 1-5 wt% and the presence of free RTIL provides for fast liquid-like diffusion and enhanced flux. This also provides an increase in mechanical and thermal properties for RTIL upon gelation.

Under a DOE funded project, University of Colorado, Boulder is working on selective layer material design and synthesis for these membranes. Fabrication of these gel-RTIL RTIL/Poly(RTIL) composite membranes by ultrasonic-atomised spray-coating is done by Los Alamos National Laboratory (LANL) and 3M. Based on the tests and results for these membranes, the Electric Power Research Institute will perform process evaluation.

IEAGHG has assessed that the use of ionic liquids has yet to be shown to offer a real advantage in a commercial system. A convincing application of this type of technology has yet to be formulated, thus the technology readiness level is assessed as TRL-2. Wood did not find any publicly available references demonstrating any further advancements in the readiness of this technology.

2.4 Solid Sorbents

Solid sorbents have been proposed for post-combustion CO₂ capture in a large number of different schemes, in circulating fluid beds, fixed beds and rotating fixed beds, employing pressure or temperature swing adsorption, chemical reaction and as supports for amines or enzymes. Solids are also used for Chemical Looping; however, this specific application is considered in Section 5 as it is also applicable in pre-combustion and oxy-combustion forms.

Pressure and temperature swing adsorption process have been in use for other applications for many years, such as for hydrogen purification and dehydration of gases. The well proven systems are mostly made up of multiple fixed beds, with one or more beds operating in adsorption mode, while other beds are being regenerated, with the number of beds related to the capacity or reliability required for the specific purpose. When such systems are applied to post-combustion CO₂ capture they are inherently challenged by the need to distribute, and often dehydrate, a large volume of hot, low pressure flue gas before feeding it to multiple trains of fixed beds. Such processes can require a lot of space and a large quantity of adsorbent in many vessels, and / or require a significant parasitic load on rotating equipment to convey the flue gas through the system.

While progress has been made, as shown below, these challenges have also prompted research into other methods of employing solid sorbents, such as using fluid beds and adding promoters to increase the amount of CO₂ that can be adsorbed per tonne of adsorbent.



61. *J.C. Anabades et al., 'Emerging CO₂ Capture Systems', International Journal of Greenhouse Gas Control, May 2015*

This paper has a broad scope but includes a useful and highly technical section covering a good range of the solid sorbent based technology variations which are being progressed. Two particularly useful reference tables are Table 11, on page 149, listing which researchers have focussed on which physical adsorption materials and Table 12, on page 150, showing which researchers have studied which amine incorporated materials.

2.4.1 Vacuum Pressure Swing Adsorption (VPSA)

62. *IEAGHG 'Assessment of Emerging CO₂ Capture Technologies and their Potential to Reduce Costs', December 2014*

This is a sub-ambient pressure variation of a pressure swing adsorption system, where the CO₂ is adsorbed at one pressure and released (as the bed is regenerated) at a lower pressure. In a typical process, first the adsorption takes place, which is followed by applying a rinse, then evacuation and purge to desorb the adsorbed gas. Mostly zeolites are used in the VPSA process, however, other improved adsorbents with a higher surface area are being developed. These include heavy metal organic framework (MOFs), zeolite imidazolate frameworks (ZIF), and carbon based materials which are less adsorptive to water. The technology is best suited to flue gases with concentrations greater than 10% in order to try and limit the necessary bed volumes.

There are two pilot plants for VPSA referred to in the IEAGHG 2014 report, one in Australia and the other in Shanghai. Major industrial gas companies, such as Air Products, Linde and UOP, are setting up VPSA plants, and a small scale adsorption process is being developed by Wartsila Hamworthy (Norway). Adsorbents such as zeolites have been developed by UOP, Grace and Zeolyte. INTF and the University of Oslo also have activities in development of improved adsorbents for CO₂ capture and an adsorption process is being developed by SINTEF. As the concept has been proven, IEAGHG still believes there is much still remaining to validate the process for CO₂ commercial use: it has therefore given the technology a TRL-3. Wood was unable to find any more recent developments in the public domain within the scope of this study, thus judges that this technology remains TRL-3.

Vacuum pressure swing adsorption has also been applied to blast furnace gas and pre-combustion schemes where it has a much higher TRL: see Section 3.4.2. It should be noted that some references discuss these pre-combustion pilots of VPSA as if they were post-combustion (such as reference 61 above). However, the stream composition and inlet pressures in the pre-combustion configuration are far less challenging and thus not comparable.

2.4.2 Temperature Swing Adsorption (TSA)

63. *IEAGHG 'Assessment of Emerging CO₂ Capture Technologies and their Potential to Reduce Costs', December 2014*

In this process, CO₂ is adsorbed at low temperature (typically 40-60°C) in the first column. The CO₂ loaded adsorbent is then transferred to a second column where it is heated to a high temperature (typically 80-150 °C) to desorb the CO₂. Alternatively, in a fixed bed scheme, the cool, CO₂ loaded bed would then be heated up using a hot gas stream, steam or electrical heating, to regenerate the bed and release the CO₂.

There is only one large pilot plant in operation since 1991, which is actually a dual PTSA process reported at the Tokyo Electric Power Company. Companies such as ARI (USA) and Inventys (Canada) have patents for a moving bed concept and a Monolith concept respectively. However, there were no large scale demonstrations for these technologies at the time of the IEAGHG 2014 report. As a sorbent with adequate performance and properties had yet to be found, the IEAGHG report gave the TSA technology a TRL-1. This seems low considering the amount of testing achieved up to 2014. Since there are two tonne per day scale pilots for different TSA technologies, it is Wood's opinion that that this technology should be rated at TRL-7.



2.4.2.1 Innosepra

64. *Innosepra Website: <http://www.innosepra.com/new-page-99/>*

This technology developer employs a fixed bed TSA scheme to remove impurities and then CO₂ from flue gases. Its largest scale demonstrator was funded by the DOE and developed with project partners DOE/NETL, NRG, EPRI, New Mexico State, PNNL and Adsorptech. The field test successfully demonstrated the process at the NRG, Indian River site producing CO₂ at greater than 90% purity and more than 90% CO₂ capture rate and 1 tonne per day scale.

2.4.2.2 Inventys

65. *Anthony Armprister (NRG Energy) and Matthew Stevenson (Inventys), 'Project CO2NCEPT', 2016 NETL CO₂ Capture Technology Project Review Meeting*

The Inventys technology is also a TSA process, but with very different physical form. This technology uses a rotary bed adsorption system, likened to the rotary air preheaters which have been employed in thermal power plants for decades. The flue gas is passed through a cold section of the adsorbent bed until that section approaches saturation. Low pressure steam is then used to release the CO₂ and regenerate that section of the bed. An air stream is used to cool the regenerated bed ready for a new cycle of CO₂ adsorption.

The rotating bed is referred to as a "rotary adsorption machine" with the trade mark "VeloXoTherm™" which resembles a disk with many segments that rotates through the three streams in sequence (flue gas, steam, air).

The presentation describes the outcome of Phase 1 NETL study, with plans for a 25 MWe demonstration unit at an NRG coal-fired power plant. A chart demonstrating 90% CO₂ purity on test runs of the Inventys demonstration plant at NRG W.A Parish are included within the presentation.

66. *Inventys Press Release: <http://inventysinc.com/2017/07/11/husky-investment/>*

The above press release announces investment agreed from Husky Energy to fund a 30 tonne per day demonstration plant on a once through steam generator (OTSG) for use in heavy oil recovery near Lloydminster, Saskatchewan, to start up in late 2018, following the successful operation of a 0.5 TPD VeloXoTherm™ pilot at the same location.

2.4.3 Molecularly Imprinted Polymer Particle CO₂ Sorbents

Wood judges that the TRL for MIPs is still TRL-1 or 2 because the work so far undertaken seems to have focussed on the formulation of the MIPs themselves, with little spent on the research needed to quantify their benefits as part of a wider process flow scheme.

67. *Seyed Ali Nabavi, Goran T. Vladislavljevic, Eseosa M. Eguagie, Beichen Li, Stella Georgiadou, Vasilije Manovic, 'Production of Spherical Mesoporous Molecularly Imprinted Polymer Particles Containing Tunable Amine Decorated Nanocavities with CO₂ Molecule Recognition Properties', Combustion and CCS Centre, Cranfield University, Department of Chemical Engineering, Loughborough University, 2016*

This paper describes the work done by Cranfield University and Loughborough University to develop spherical poly(AAm-co-EGDMA) particles with CO₂ recognition cavities. In this work, novel spherical acrylamide-based MIP particles for CO₂ capture were fabricated by suspension polymerisation in an oil-in-water emulsion. In suspension polymerisation, each monomer droplet acts as a tiny batch reactor, which facilitates heat transfer and thus the polymerisation occurs faster and the final conversion of the monomer can reach higher values.

Polymer-based materials such as porous aromatic frameworks (PAFs), hyper cross-linked polymers (HCPs), and covalent organic polymers (COPs) are a new class of CO₂ sorbent characterised by high selectivity and CO₂ uptake, hydrothermal stability and ease of structural modification.



For this project, amide-decorated nanocavities were created by crosslinking acrylamide in the presence of oxalic acid, followed by extraction of the dummy template to expose nanocavities. The particles were inherently amide-functionalised and there was no need for amine grafting to increase CO₂ adsorption capacity. Due to CO₂-philic moieties on the walls of the cavities and their shape, which is complementary to CO₂ molecules, the particles are highly selective to CO₂. They are suitable for use in fluidised bed reactors, because of their tunable diameter greater than 100 µm and relatively high density.

68. *Xiaochun Xu, Chunshan Song, John M. Andresen, Bruce G. Miller, Alan W. Scaroni, 'Preparation and Characterization of Novel CO₂ "Molecular Basket" Adsorbents based on Polymer-Modified Mesoporous Molecular Sieve MCM-41', The Pennsylvania State University, 2003*

This report describes the process to create novel CO₂ "molecular basket" adsorbents, which were prepared by synthesising and modifying the mesoporous molecular sieve of MCM-41 type with polyethylenimine (PEI). Using polyethylene glycol as an additive into the MCM-41-PEI adsorbent increased not only the CO₂ adsorption capacity, but also the rates of CO₂ adsorption / desorption. At PEI loading of 50 wt% in MCM-41-PEI, the highest CO₂ adsorption capacity of 246 mg/g PEI was obtained, which is 30 times greater than that of the MCM-41 and is about 2.3 times that of the pure PEI.

69. *Stephen R. Caskey, Antek G. Wong-Foy and Adam J. Matzger, 'Dramatic Tuning of Carbon Dioxide Uptake via Metal Substitution in a Coordination Polymer with Cylindrical Pores', The University of Michigan, 2008*

This study looked at a series of four isostructural microporous coordination polymers (MCPs) which differed in metal composition and demonstrated exceptional uptake of CO₂ at low pressures and ambient temperature at conditions particularly relevant for capture of flue gas from coal-fired power plants. A magnesium-based material is presented that is the highest surface area magnesium MCP yet reported and displays ultra-high affinity based on heat of adsorption for CO₂. The study demonstrated that physisorptive materials can achieve affinities and capacities competitive with amine sorbents at greatly reduced regeneration energy.

2.4.3.1 Cambridge Engineering Analysis and Design (CEAD): Molecular Imprinted Polymer Sorbents Technology

70. *Cambridge Engineering Analysis and Design Website:*
<http://www.ceadltd.co.uk/index.php/portfolio/coerce>

The Cambridge Engineering Analysis and Design Website has a page on their CoERCe (Combined Energy Recovery and Carbon Capture) project. CoERCe was a project to establish the feasibility of a novel polymer based carbon dioxide adsorbent. This was a 12-month project and involved collaboration with European Thermodynamics Laboratory, Loughborough University and Cranfield University. The project was supported by Innovate UK through the Energy Catalyst 3 programme. The project accelerated the development of the polymer based adsorbent materials culminating in a patent application. A bench top adsorption-desorption test rig was constructed and used for testing the materials as part of the programme.

71. *Innovate UK, 'Innovation', Slide 16 'Cleantech Collaboration Nation Project Directory-FINAL 11.2.16'*

These slides introduce the CEAD (Cambridge Engineering Analysis and Design) CoERCe project. The slides state that the CoERCe project addresses three main challenges associated with carbon capture industry: (i) cost reduction, (ii) reduction of emissions and (iii) security of supply.

Their CO₂ adsorption technology is said to consist of a solid CO₂ adsorbent. The advantage of the novel solid CO₂ sorbent material is its low cost, ability to be mass produced and lower energy input to recover the CO₂ compared with conventional processes. The next steps of the project are to produce scaled-up prototype of CoERCe system that captures and removes CO₂ emissions within a real application, either on biomass generators or existing fossil fuels process plant.



2.4.4 Amine Catalysed Adsorption

A number of technology developers are making use of the chemical affinity of amines with CO₂ combined with a solid adsorbent.

72. Takeshi Okumura, 'Study on Solid Adsorbent for CO₂-Capture from Post Combustion Gases Utilizing Low-Temperature Thermal Energy: 2nd Post Combustion Capture Conference', Kawasaki Heavy Industries, Ltd. (Japan), 2013

Kawasaki have developed a solid adsorbent, made from an amine-coated porous material that enables selective CO₂ adsorption for post-combustion gases. They have called their technology Kawasaki CO₂ Capture (KCC). In lab tests, the company claims that it has seen 'superior' adsorption performance for CO₂ concentration between 0.1% and 50%, which would enable the technology to be used for a wide range of applications. Kawasaki has also tested the technology at a 10 tonne CO₂ per day test plant, on coal fired flue gas. The test results claim that half the thermal energy is required for its KCC CO₂ capture compared with MEA. The adsorbent is regenerated using 60°C steam. The slides state that Kawasaki wishes to begin commercialising its 'KCC Moving-Bed System' at the beginning of 2016. They have completed a feasibility study for a cement plant and gas engine KCC application. The feasibility study found that CO₂ capture energy is 1.6 GJ/t-CO₂ for the cement plant and 1.3 GJ/t-CO₂ for the gas engine.

Since Kawasaki has an operating 10 TPD plant, Wood concludes that the amine catalysed adsorption process has reached TRL-6.

2.4.5 Electrochemically Mediated Adsorption

As this technology is at a very early stage of development and only the basic principles and concept have been researched, the IEAGHG assessed that the technology is at TRL-1 in 2014. Subject to the research outlined below, it is anticipated that electrochemically mediated adsorption is now at a higher TRL, possibly up to TRL 6, but it was not possible for Wood to confirm this using publicly available reference material.

73. IEAGHG 'Assessment of Emerging CO₂ Capture Technologies and their Potential to Reduce Costs', December 2014

In this process, the CO₂ reacts with an amine and it is subsequently decomposed in an electrochemical cell in a process similar to electrolysis, rather than in a reboiler. The reboiler and stripper in the amine regeneration system is replaced with an electrochemical cell, thus reducing the energy penalty and solvent thermal regeneration. In the electrochemical cell, the transfer of the electrons is between the metal and its cation. The cation has a greater affinity for the amine than the CO₂ which is thus released. The metal ions of higher oxidation state are formed at the anode where they displace the CO₂ from the amine / CO₂ complex. The metal ion amine complex which results is then reduced at the cathode to regenerate the amine which can then absorb more CO₂.

The IEAGHG report states that a number of groups are researching electrochemically mediated amine systems. Massachusetts Institute of Technology has tested its electrochemically mediated amine technology at bench scale. Siemens and Topchiev Institute of Petrochemical Synthesis, Russia are also considering this technology.

2.4.5.1 Future Environmental Technologies

74. Project Coral – Integrated CHP, carbon water exchange Pilot Demonstration: Pilot Scale Demonstration, November 2012 - April 2015

There is a reference to a pilot demonstration which appears to be electrochemically mediated adsorption on the UKCCSRC website, but no further information could be found relating to the project at the time of writing.

2.4.6 Mineral Carbonation

The mineral carbonation process appears somewhat like a solid adsorption process in some ways. However, the CO₂ reacts with the calcium-containing contact material to form a solid carbonate via



chemical reaction. Unlike any of the above processes, the material is not then regenerated to release the CO₂, but the CO₂ is kept permanently in the solid carbonate form. This method is particularly applicable when waste streams are employed as the calcium or magnesium bearing material and are more challenged if it is assumed that the feed material is mined, transported, crushed and activated for the sole purpose of CO₂ capture.

75. *Omeid Rahmani, Radzuan Junin, Mark Tyrer and Rahmat Mohsin, 'Mineral Carbonation of Red Gypsum for CO₂ Sequestration', Universiti Teknologi Malaysia, Mineral Industry Research Organisation (UK), 2014*

This research tested the feasibility of CO₂ mineral carbonation using red gypsum, as the calcium rich source using an autoclave mini reactor. The effect on the rate of mineral carbonation for a wide range of variables was studied, such as reaction temperature, reaction time, CO₂ pressure, and liquid / solid ratio. The results showed that the maximum conversion of calcium (98.8%) was obtained at the condition that had an optimum balance of these variables. The results confirmed that red gypsum has high potential to form calcium carbonate (CaCO₃) during the process of CO₂ mineral carbonation. It concluded that the mineral carbonation process using red gypsum can be considered to be an interesting, applicable, and low-cost method of CO₂ capture.

76. *Myung Gyu Lee, Kyung Won Ryu, Soo Chun Chae & Young Nam Jang, 'Effects of Temperature on the Carbonation of Flue Gas Desulphurization Gypsum using a CO₂ / N₂ Gas Mixture', Korea Institute of Geoscience and Mineral Resources, Chungbuk National University Korea, 2015*

This paper also focussed on using flue gas desulphurisation produced gypsum for mineral carbonation CO₂ capture. The research used a CO₂ / N₂ gas mixture to study the feasibility of using the flue gas directly in the gypsum carbonation. The effect of the reaction temperature on the carbonation reaction and the carbonation conversion efficiency was considered. The carbonation conversion efficiency was calculated using a new method for decreasing the error range from a sample containing unreacted gypsum.

It was found that at 40°C, the reaction was twice as fast, whilst the carbonation conversion efficiency (96%) was nearly the same as the same reaction at room temperature. However, the efficiency decreased significantly with temperature, especially above 60°C. It can therefore be concluded that the direct use of flue gas in gypsum carbonation is most feasible at around 40°C.

The temperature of carbonation was found to strongly affect the shape of the CaCO₃ polymorphs. Calcite with various shapes was the dominant phase (40–90%) at all temperatures. At temperatures below 40°C, spherical-shaped vaterite was pronounced, while needle-flower-shaped aragonite was dominant at temperatures above 80°C.

77. *G.Hillier (CPI), M. Styles (BGS), S. Zemskova (UoN), T. Paulson (Caterpillar); "Carbon Capture and Sequestration by Mineralisation (CCSM) Final Report", Energy Technologies Institute (ETI), 2012*

This report to DECC from the ETI summarises a body of work on Mineral Carbonation of CO₂ for CO₂ storage (CCSM) undertaken by a consortium including Caterpillar, Perkins Engines Company Limited, Shell Global Solutions International B.V., Natural Environment Research Council as represented by the British Geological Survey, and the University of Nottingham. The report mainly presents conclusions for the scale-up of the Shell direct single step aqueous carbonation process (with additives), which is relatively well developed, and a multi-step indirect aqueous carbonation process using ammonium developed by the consortium. The Shell process was found to have a specific cost of CO₂ capture approximately double that of conventional CCS, while the ammonium based process required so much energy for ammonium salt recovery that the process resulted in an increase in the total CO₂ from the base plant.

The report concluded that although the concept of permanent stable storage of CO₂ in carbonate form is attractive, the energy and processing required to achieve it makes the CCSM option infeasible in all but a few very specific applications.



2.4.6.1 Carbon Cycle: Mineral Carbonation Technology

78. 'Commercializing Carbon Capture', Carbon Cycle:

<https://www.nepic.co.uk/wp-content/uploads/2016/09/DSevier-CarbonCycle.pdf>

This document presents an overview of the Carbon Cycle's mineral carbonation technology. Interestingly, the technology can be used for flue gas as low as 3% CO₂, and biofuel fired power plants. It states that virtually any combustion emission stream should potentially work with the process.

The open cycle reaction is shown below:



(Gypsum) (Carbon dioxide) (Ammonia) (Water) (Calcium carbonate) (Water) (Ammonium sulphate)

The document states that the process has the following advantages:

- Output markets measured in tens of millions of tons.
- Reaction happens at ambient temperatures.
- Current routes to make precipitated calcium carbonates are very energy intensive.
- Current processes to make ammonium sulphate except as a neutralisation by-product are expensive.
- The reaction products and starting materials are straightforward to separate and conserve.
- Gypsum is a widely available and a common soft mineral of low value.
- The reaction works at all carbon dioxide concentrations, including that in air. Most carbon capture processes become highly inefficient at low carbon dioxide concentrations.
- Calcium carbonate or chalk is a very stable carbon sink that nature has used for millions of years for carbon dioxide.

Carbon Cycle states that there is strong demand for calcium carbonate and ammonia sulphate, which they expect to grow in the future. The technology has been demonstrated on commercial operation of carbon capture at gas plant emission CO₂ concentrations (3%). It has also demonstrated carbon capture scrubbing down to 3000 ppm CO₂.

79. Patent: <https://www.google.com/patents/WO2012013961A2?cl=en>

The patent describes using a bubble tower for Carbon Cycle's CO₂ separation process.

Carbon Cycle Limited's website appears to market its technology as a method of purification of gypsum and chalk while reclaiming precious metals and achieving high purity gypsum and chalk.

While reference 78 states that there has been a commercial demonstration of the Carbon Cycle Technology, there is no reference to this on their website, which suggests this was a small scale test at the site, rather than a commercial plant. If this assumption is correct then Wood judges this technology may now be at TRL-5.

2.5 Physical Separation

2.5.1 Cryogenic Capture

Much of the research described below is focussed on thermodynamics and simulation. However, the creation and operation of a fully functioning prototype at bench scale leads Wood to conclude that this technology is currently at TRL-4.



80. *IEAGHG 'Assessment of Emerging CO₂ Capture Technologies and their Potential to Reduce Costs', December 2014*

A number of groups have developed processes involving the “desublimation” or freeze-out of CO₂. There are different processes presented in the IEAGHG report by Clodic et al 2002 and General Electric. However, the focus is on the Clodic process. A series of heat exchangers are used to cool the flue gas down to -56 / -40°C. This solidifies the CO₂, allowing it to be physically separated. The advantage of this technology is the claim of negligible environmental impact due to there being no chemicals involved (presumably excluding the source of low temperature).

Clodic et al 2011 performed a pilot plant test, and GE has evaluated its technology on the basis of simulation work. Other companies involved in the development of this technology are Shell Global Solutions, Alstom, Ereie, University of Eindhoven and MINES ParisTech. As the principles of this technology have been validated in a small scale laboratory environment, the IEAGHG has assessed the technology at TRL-3. However, as many of the heat exchanger and refrigeration systems are based on well-developed design and construction principles, the IEAGHG believe that development and commercialisation could proceed very quickly.

81. *Mark Jensen “Energy Process Enabled by Cryogenic Carbon Capture”, Brigham Young University – Provo, 2015*

This is a dissertation submitted to the faculty of Brigham Young University. The paper presents the results from bench scale experiments on cryogenic carbon capture. The skid scale experiments demonstrated the feasibility of the critical CO₂ desublimation in a direct contact heat exchanger, which is a crucial item of equipment in the SES process.

This paper has done a full scale simulation for External Cooling Loop Cryogenic Carbon Capture (CCC ECL process) for coal fired power plant and a basic energy balance and mass balance is presented. The report states that CCC ECL is capable of 90 % CO₂ capture with a simulated energy penalty of 0.74 MJe/kg CO₂. The report also presents the results of the economic analysis for a 90% CO₂ capture rate.

82. *Seyed Mostafa Safdarnejad, John D. Hedengren, Larry L. Baxter “Plant-level Dynamic Optimization of Cryogenic Carbon Capture with Conventional and Renewable Power Sources”, Department of Chemical Engineering, Brigham Young University, 2015*

This paper looks at using the energy storage capacity of Cryogenic Carbon Capture (CCC) to shift the parasitic loss of the CCC away from peak hours. The report describes the process for modelling the CCC and power production systems. The CCC process modelled is a retrofit, post-combustion technology that captures CO₂ in the flue gas through desublimation. The resulting solid is separated from the remaining light gases. Solid CO₂ is then melted, pressurised, and transported to underground containment wells. The CCC process requires two refrigeration loops that consume most of the energy in running the compressors. However, refrigerant can be generated during non-peak hours and stored in insulated vessels that save the refrigerant for peak hour usage, thereby replacing the compressor energy with the stored refrigerant. This causes the refrigerant production rate to decrease during peak hours, which decreases the energy demand required by the CCC for as long as the stored refrigerant is available. Therefore, more power is available during peak hours relative to the baseline coal boiler rated capacity.

83. *Larry Baxter, “Cryogenic Carbon Capture as a Holistic Approach to a Low-Emissions Energy System”, Department of Chemical Engineering, Brigham Young University, 2015*

The paper is a summary of the Mark Jensen 2015 paper, reference 82, above.

84. *Sustainable Energy Solutions “Cryogenic Carbon Capture University of Wyoming Bench Scale Project”, 2009*

This source presents the Wyoming Bench-Scale Cryogenic Carbon Capture (CCC) Project. The four aims of the project were: (1) process flow analysis, (2) heat exchanger analysis and design, (3) bench scale design, and (4) completion of a fully integrated bench scale demonstration unit.



Completing these four tasks produced the first fully integrated CCC process unit, while making significant improvements to the design of the CCC process by solving specific challenges associated with efficient heat exchange. The bench-scale CCC process was run for 2 hours to demonstrate the CO₂ and SO₂ capture efficiencies. The CO₂ capture efficiency was between 93 - 94% for runs 1 and 2. A bench-scale CCC process was run for 3 hours to further demonstrate the CO₂ capture efficiency with an average of 95%. During these experiments, there was no indication of process degradation. The bench-scale experiments have helped prove various systems that will be incorporated into the skid-scale, pilot-scale, and full-scale processes. Many parts of the electrical and control systems were first prototyped on the bench-scale process and are now being incorporated into the skid-scale process.

85. *Gang Xu, Feifei Liang, Yongping Yang, Yue Hu, Kai Zhang and Wenyi Liu 'An Improved CO₂ Separation and Purification System Based on Cryogenic Separation and Distillation Theory', Beijing Key Laboratory of Emission Surveillance and Control for Thermal Power Generation, School of Energy Power & Mechanical Engineering, North China Electric Power University, 2014*

In this study, an improved CO₂ separation and purification system is proposed based on in-depth analyses of cryogenic separation and distillation theory as well as the phase transition characteristics of gas mixtures containing CO₂. Multi-stage compression, refrigeration and separation are adopted to separate the majority of the CO₂ from the gas mixture with relatively low energy penalty and high purity. Subsequently, the separated crude liquid CO₂ is distilled under high pressure and near ambient temperature conditions so that low energy penalty purification is achieved. Simulation results indicate that the specific energy consumption for CO₂ capture is only 0.425 MJ/kgCO₂ with 99.9% CO₂ purity for the product.

86. *US Patent 8764885 B2: 'Systems and Methods for Separating Condensable Vapors from Gases by Direct-Contact Heat Exchange'*

The SES patent describes the process, operating parameters and criteria for selecting a non-volatile heat exchange liquid.

2.5.2 Supersonic Inertia Capture

The IEAGHG had given this technology a readiness level of TRL-1. Given that components of the technology have been tested at bench scale, Wood judges that it has now progressed to TRL-3.

87. *IEAGHG 'Assessment of Emerging CO₂ Capture Technologies and their Potential to Reduce Costs', December 2014*

The inertial CO₂ extraction system (ICES) involves direct flue gas from a coal fired power plant to a converging diverging nozzle and then expanding the flue gas to supersonic velocities. The process of aerodynamic expansion to high velocity results in the conversion of potential energy contained in the form of temperature and pressure to kinetic energy. The rapid temperature and pressure decrease produced from this conversion results in the condensation of the undesirable constituents of flue gas, including the desublimation of the CO₂. The high density of the solid phase constituents of the flow allows the inertial separation by centrifugal forces induced by the flow path curvature. The advantages of this process are that no chemicals are required, and due to the high flow velocity, it has a very small system volume (compared to membrane systems).

Alliant Techsystems Operations and ACENT laboratories have teamed with the Electric Power Research Institute and the Ohio State University for further development of the technology for post combustion CO₂ capture. DOE funded research generated CO₂ particles greater than 2.5 µm in effective diameter to ensure efficient inertial migration. The current DOE project is focused on verification of CO₂ particle growth to a size that permits them to migrate to a compact layer adjacent to one wall where they can be readily removed by a boundary layer. The principle of inertial separation using supersonic flows is proven and commercialised in another application.



88. *Jonathan Forsyth, Stuart Lodge, Stefano Consonni, Daniele Di Bona, Manuele Gatti, Emanuele Martelli, Roberto Scaccabarozzi, Federico Viganò, 'Evaluation of five alternative CO₂ capture technologies with insights to inform further development: 13th International Conference on Greenhouse Gas Control Technologies, GHGT-13, 14-18 November 2016, Lausanne, Switzerland', BP International Limited, Consorzio LEAP – Laboratorio Energia e Ambiente Piacenza, November 2016*

Supersonic flow-driven CO₂ deposition was also considered by CCP as one of five alternative technologies suitable for post combustion CO₂ capture from natural gas derived exhaust gases, as documented in the above paper. This study performed some very high level performance and costing, but concluded that more data was needed before confidence could really be placed in the results.

89. *Anthony Castrogiovanni, Vladimir Balepin, Andrew Robertson, Bon Calayag, 'Supersonic Post-Combustion Inertial CO₂ Extraction System Bench Scale Project Status Update', 2016 NETL CO₂ Capture Technology Meeting, Pittsburgh, August 2016*

This presentation summarises the results of bench-scale tests of a subsonic expansion tube at the Orbital ATK laboratory. The tests were designed to assess the size range of condensed CO₂ particles using laser imaging and to measure pressure recovery in the expansion zone. Further work was envisaged through to the end of 2017 to increase the condensed particle size, improve particle capture rates and to improve the overall system efficiency.



3 Pre-Combustion Capture

3.1 Overview

Pre-combustion capture refers generally to capture of carbon dioxide before combustion has taken place. Although the definition implies that there is always combustion involved in the overall system, it is a loose term which includes similar processes in which there is no downstream combustion, such as the acid gas removal step of natural gas treating, pre-treatment for liquefied natural gas (LNG), syngas conditioning and hydrogen purification. It also makes sense to include within this group processes in which the gas being treated is similar in composition and pressure to a syngas stream, such as blast furnace gas.

While the main area for improvements to post-combustion CO₂ capture schemes lie within the CO₂ separation unit itself, in pre-combustion schemes, including integrated gasification combined cycles and integrated reforming combined cycles, there are some major areas for further improvement in units other than the CO₂ capture step, such as the high hydrogen gas turbines, air separation and the gasifier itself. However, these other units are considered outside of the scope of this study, which will focus on the technology improvements for the CO₂ removal step, and when appropriate, the shift step.

The 2014 IEAGHG report has given each of the pre-combustion capture technologies researched in this literature review a Technology Readiness Level (TRL). Further development has been conducted for many of these technologies since that time. The following table summarises TRL's given to each technology by the IEAGHG in 2014 alongside the 2017 TRL estimated by Wood resulting from the literature review.

Table 3-1: TRL for Pre-Combustion Capture Technologies

Technology	2014 TRL	2017 TRL
Conventional Solvents for Natural Gas Treating	9	9
Conventional Solvents for Hydrogen Purification *	-	9
Gas Separation Membranes for Natural Gas Treating *	-	8
Gas Separation Membranes	5	5
Physical Separation	2	7
Pressure Swing Adsorption *	-	9
Vacuum Swing Adsorption *	-	8
Low Temperature Separation of CO ₂ from Natural Gas *	-	7
Low Temperature Separation of Syngas	2	2

* These technologies were not assessed in the IEAGHG 2014 report.

3.2 Solvents

3.2.1 Conventional Solvents for Natural Gas and Syngas Treating

The removal of sour and acid species from natural gas has developed significantly over six decades and the technologies used are also applicable to the removal of H₂S and CO₂ from syngas. While conventional technology developments are not included within the scope of this review, the following description of development is included to demonstrate the level of competitiveness and experience already achieved in that market space.

Large scale treatment plants invariably use regenerable solvent technologies. Regenerable solvent technologies can be broadly grouped into chemical and physical solvents and combinations called hybrid solvents.



3.2.1.1 Chemical Absorption

In chemical absorption, acid gas components (CO₂ and H₂S) in the gas stream dissolve in the solvent within the absorber column and are held in aqueous solution by ionic balance with the dissociated solvent ions.

The main advantage of chemical absorption is that the formation of chemical bonds (ions in solution which behave like bonds) between the acid gas and the solvent largely prevent migration of the acid gas from the solvent back into the gas phase. This allows very low acid gas levels to be achieved in the treated gas. The associated disadvantage of chemical absorption is that breaking the bonds between the acid gas and solvent in the regenerator column is energy intensive, requiring a lot of heat input. Moreover, the characteristics allowing formation of bonds with acid gas tend to make chemical solvents susceptible to degradation by contaminants in the feed gas.

Chemical absorption is the most common and most well-established technology used for industrial scale acid gas removal and is almost always the selected technology for applications which require a very low (50ppmv) level of CO₂ or H₂S in the treated gas stream. The technology is popular as it offers reliable operation throughout the lifetime of the plant and operates over a wide range of process pressures.

Three types of amines are used commercially for gas treating:

- Primary amines, such as monoethanolamine (MEA) and diglycolamine (DGA®) with one hydrocarbon chain connected to the amine group;
- Secondary amines, such as diethanolamine (DEA) and diisopropanolamine (DIPA), with two hydrocarbon chains connected to the amine group;
- Tertiary amines, such as methyl diethanolamine (MDEA), with three hydrocarbon chains connected to the amine group.

Amines form a reversible reaction with acid gases such as H₂S and CO₂. Primary amines forming the most stable bond, and tertiary amines the least stable. MEA was used extensively in the gas processing industry but has been displaced by DEA and tertiary amines due to their lower corrosivity, lower energy requirement to strip acid gas from the amine, and higher achievable acid gas loadings (moles of acid gas absorbed per mole of solvent in circulation, leading to lower solvent circulation rates).

Table 3-2: Comparison of Amines

	MEA	DEA	MDEA
Typical Amine Concentration (wt%)	20	35	50
Acid Gas Capacity (kmol / kmol amine)	0.35	0.4	0.5
Stripping Energy (MJ/m ³ solvent)	280-335	235-280	220-250

Monoethanolamine, MEA

Monoethanolamine (MEA) has been widely used in acid gas removal service for over 60 years and so its chemistry is well known. MEA is a primary amine with high reactivity to acid gases and its purchase cost is inexpensive when compared to other amines. Although MEA is susceptible to degradation by acidic species such as hydrogen cyanide (HCN) and chlorides, the solvent can be reclaimed by heating with a strong alkali solution.

The main disadvantage of MEA is that a large amount of energy is required to strip the acid gases from the rich solvent solution due to the strength of the chemical bonds. It also has a high vapour pressure, so is usually diluted to at least 25% concentration by weight, reducing the quantity of acid gas that can be absorbed per unit volume and therefore requiring high solvent circulation rates. MEA also co-absorbs benzene, toluene and xylenes (BTX) and is degraded by the presence of any



carbonyl sulphide or carbon disulphide in the feed gas. When the solvent reacts with these contaminants to form degradation products, these materials are highly corrosive.

Diethanolamine, DEA

Diethanolamine (DEA) is a secondary amine mainly used in refinery operations. As a secondary amine, DEA has a lower vapour pressure and lower strength of absorption than MEA or DGA®. This results in lower solvent losses and lower energy input to strip acid gases from the rich solvent.

On the negative side, DEA has a lower CO₂ absorption capacity than MEA. CO₂-rich DEA is less corrosive than CO₂-rich MEA, but more corrosive than MDEA, and degraded DEA cannot be thermally reclaimed.

DEA was used extensively as an AGRU solvent in older LNG facilities, but more recent projects have generally used tertiary amine solvents such as MDEA.

Diisopropanolamine, DIPA

DIPA, like DEA, is a secondary amine. While its field of application is similar to DEA, DIPA degrades in the presence of CO₂, so is not recommended in services with high CO₂ concentration.

Methyldiethanolamine, MDEA

MDEA is a tertiary amine. It is particularly stable and thus more resistant to degradation than other amines (except in the presence of oxygen and is therefore not suitable for flue gases). It has a low vapour pressure and low corrosivity which allow its use at high solvent concentrations.

As a tertiary amine, MDEA forms weaker bonds with acid gas than primary and secondary amines, leading to lower stripping energy requirements.

While MDEA solutions can achieve high acid gas loadings, the reaction rate is slow for CO₂ and so aqueous MDEA on its own is not generally used for CO₂ removal down to low levels. However, the rate of reaction can be increased significantly by the addition of reaction activators. For this reason, MDEA is usually used in combination with an activator as a formulated MDEA (see below). Note that formulated MDEA refers to all types of formulation, for all types of gas treating purposes.

Another disadvantage of MDEA is that it has a tendency to foam, particularly in the presence of long chain hydrocarbons in the gas feed, thus this not such a problem for a syngas. Anti-foaming agents are often used to suppress this foaming, which can otherwise cause carryover of amine into downstream units.

Diglycolamine, DGA®

DGA® (Diglycolamine) is a primary amine that competes with MEA. DGA, however, has a lower vapour pressure and can be operated at 50% concentration by weight, providing more CO₂ absorption capacity per unit volume of solvent. The low freezing point of the solution (a 50 wt% DGA solution has a freezing point of -35°C) offers an advantage over the other amine solutions especially in cold weather areas.

Although DGA® has a number of advantages relative to MEA, it shares the primary amine disadvantage of high stripping power requirement and has largely been superseded by tertiary amines such as MDEA.

Formulated MDEA

Formulated MDEAs consist of MDEA and a reaction activator. They provide MDEA's benefits of low rate of degradation, low corrosivity, low stripping energy and high acid gas capacity while overcoming MDEA's low rate of reaction with acid gases. Use of formulated MDEAs results in lower solvent circulation rates and energy consumption than other amine options, making much of the AGRU equipment smaller.

Several of the main solvent manufacturers have developed formulated solvents based on MDEA with a promoter. These solvents inherit a resistance to degradation from MDEA.



Formulated amine systems available as a licensed FEED package include:

- OASE from BASF.
- UCARSOLTM from UOP.
- ADIP-X from Shell, which uses piperazine.

A process based upon Shell ADIP-X is used to capture more than 1 MTPA of CO₂ from steam methane reformers at the Shell Quest project which has been operating in Canada since late 2015.

Formulated amines are also available as proprietary solvents, for which the engineering contractor would undertake the design and development of the AGRU based upon very high level information from the solvent vendor. These include:

- UCARSOLTM from DOW.
- GAS/SPEC from Ineos.
- JEFFTREAT® from Huntsman Corp.

Of the technologies listed above, Shell, UOP and BASF lead in terms of reference plants and experience.

3.2.1.2 Physical Absorption

90. *B. Burr & L. Lyddon, Bryan Research & Engineering, "A comparison of physical solvents for acid gas removal", <https://bre.com/PDF/A-Comparison-of-Physical-Solvents-for-Acid-Gas-Removal-REVISED.pdf>*

This paper provides a good overview of the various physical solvents which can be applied for acid gas removal.

Physical solvents absorb the acid gas physically rather than chemically and they tend to be favourable over chemical solvents when the partial pressure of acid gases is very high. The benefit of physical solvents over chemical solvents is that they are less energy intensive to regenerate (usually pressure reduction is sufficient to release the acid gas without steam stripping), they are generally non-corrosive and they are more resistant to degradation. The disadvantage of physical solvents is that because the acid gas is not as strongly held by the solvent it can migrate back into the treated gas from the lean solvent, making it more difficult to achieve very low acid gas levels in the treated gas.

Physical solvent processes are generally only recommended for reducing acid gas concentrations from very high levels to moderate levels and are often chosen for gasification system designs. Physical solvents are also more prone to co-absorption of hydrocarbons, making them less suitable for natural gas treating, particularly for rich natural gases, which is not usually a problem for syngas applications.

Physical solvents processes technologies include:

- Selexol (UOP).
- Rectisol (Linde and Lurgi);
- IFPexol (IFP);
- Purisol (Lurgi);
- Fluor Solvent (Fluor),

Selexol

Selexol is composed of dimethyl ethers and polyethylene glycols (DEPG). The Selexol process is licensed by UOP and is highly selective, delivering separate H₂S and CO₂ rich streams while also removing mercaptans. Physical solvents generally require less energy for regeneration than



chemical solvents and this also applies to the Selexol process, as long as the feed gas pressure is above about 20 bar (abs).

Rectisol

Rectisol is licensed by both Linde and Lurgi. It uses a methanol based solvent at sub-ambient temperatures. Its main advantage is that while it is selective and removes carbonyl sulphide, the main component of the solvent is cheap compared to Selexol.

Although the energy required for solvent regeneration is low compared to an amine system, the Rectisol system has a high electrical parasitic load due to the need for a refrigeration system. This also contributes to a higher capital cost than other systems.

IFPexol

IFPexol is also a methanol based solvent. The two stage IFPexol process can be applied to natural gas treating as the first stage removes the heavy hydrocarbons and water.

Purisol

This process uses N-Methyl-2-Pyrrolidone (NMP) and is also licensed by Lurgi. NMP has the benefit of simultaneous dehydration with acid gas removal but its high vapour pressure requires solvent recovery on all streams exiting the unit.

Fluor Solvent

The Fluor Solvent process uses propylene carbonate (PC) and has the particular advantage in very low H₂S syngas service that it has a lower solubility of light hydrocarbons and hydrogen, reducing the recycle gas flow and hydrocarbon and hydrogen slip to the CO₂ stream.

3.2.1.3 Hybrid Regenerable Solvent Technology

Hybrid regenerable solvent technology is the name given to mixed solvent systems comprising a chemical and physical solvent component formulation in aqueous solution. The chemical solvent allows low acid gas concentrations to be achieved in the treated gas, while the physical solvent increases the acid gas removal capacity of the solvent. In general, physical-chemical solvents aim to combine the advantages of both solvent types with tailored composition for specific purposes.

The Shell Sulfinol process employs physical-chemical solvent formulations. Some formulated MDEA solvents also feature a physical solvent in the formulation, for example some types of UCARSOL.

The Sulfinol process, licensed by Shell, uses physical-chemical solvents where sulfolane is the physical solvent component and MDEA or DIPA are the chemical solvent component:

- Sulfinol-D is DIPA, sulfolane and water;
- Sulfinol-M is MDEA, sulfolane and water
- Sulfinol-X is MDEA, sulfolane, water and an activator (piperazine)

The Sulfinol flow scheme is similar to a conventional amine absorber stripper scheme, but an additional heater (a reclaimer) is required to address degradation of the solvent.

The Sulfinol process is one of the more common acid gas removal technologies, typically applied to LNG liquefaction pre-treatment and gas plants with higher sulphur feed gases. One of the benefits of the Sulfinol process is that it is capable of removing mercaptans and carbonyl sulphide as well as H₂S and CO₂.

3.2.1.4 Conventional Natural Gas Treating Solvents Conclusion

All of the above solvents and processes used in natural gas treating are extensively demonstrated and have undergone years, or decades, of development and refinement by their parent companies into refinement of both the solvents and their processes. It is Wood's view is that incremental further improvements in performance can be expected from conventional proprietary solvents but



that step changes in improvement are unlikely. This is also a highly competitive market that would be challenging for new entrants.

In Wood's recent experience, an activated MDEA or related solvent is generally selected for LNG pre-treatment or natural gas based pre-combustion syngas treatment while either Rectisol or Selexol have been selected for IGCC schemes, and coal or heavy fuel oil based ammonia, methanol, synthetic natural gas and Fischer-Tropsch plants. Pressure swing adsorption is the most frequent method of hydrogen purification within recent refinery based steam methane reforming based hydrogen production units (see section 3.4).

3.2.2 UOP Benfield Process

The Benfield Process has been in commercial use for many decades and has a TRL of 9.

91. *UOP LLC, A Honeywell Company, 'UOP Benfield™ Process Low cost removal of CO₂ and H₂S from natural and synthesis gas', 2013*

Originally developed at the US Bureau of Mines in the early 1950s, the hot potassium carbonate (HPC) process has been modified and optimised by Benson and Field and, subsequently, UOP. This process has been used extensively for the removal of acid gases from syngas, particularly in hydrogen production units.

The UOP Benfield Process is a thermally regenerated cyclical solvent process using an activated, inhibited hot potassium carbonate solution to remove CO₂, H₂S and other acid gas components. More than 700 Benfield units have been put into commercial service. While not an amine-based process, this technology has been in use for decades, thus cannot be considered a "novel solvent" for CO₂ removal.

A number of process variations have been developed by UOP. The UOP Benfield ACT-1™ activator process used an activator to increase the mass transfer rates of CO₂ absorption using hot potassium carbonate solutions. The UOP Benfield LoHeat™ technology is a near-isothermal Benfield unit operation that uses a flash drum with a range of configurations to progressively increase energy savings at the expense of capital increases. Finally, the UOP proprietary packing process uses hot potassium carbonate with the tower internals from Raschig that have been designed to allow higher feed gas rates and therefore provide higher throughputs.

92. *O. Eisa, and M. Shuhaimi, 'Thermodynamic Study of Hot Potassium Carbonate Solution Using Aspen Plus', 2010*

This paper presents a study on the thermodynamics and transport properties of the Benfield solvent. The disadvantages of the hot potassium carbonate are listed in the paper as carbon steel corrosion, which is caused by potassium carbonate solution, and precipitation of the solvent, where crystal accumulations and fouling can cause blockages in the Benfield reboiler system and pipeline.

3.3 Membranes

3.3.1 Membranes for CO₂ Capture from Syngas

It is Wood's view that membrane use for pre-combustion CO₂ capture remains at TR-5, although it is worth noting that membranes for use in natural gas treating are demonstrated at scale and thus should be considered TR-8.

93. *IEAGHG 'Assessment of Emerging CO₂ Capture Technologies and their Potential to Reduce Costs', December 2014*

For CO₂ capture from pre-combustion CO₂ systems, membranes can be placed at several stages in the IGCC or reforming scheme in order to assist the shift reaction (by removing one species from the reaction zone). Such membranes will have to withstand high temperatures, unless placed a long way downstream of the shift, and can be either H₂ membranes or CO₂ membranes.



Various types of membranes are currently available for pre-combustion capture. These include porous inorganic membranes, palladium membranes, polymeric membranes and zeolites. There are two main types: hydrogen membranes whereby hydrogen selectively passes through the membrane, and CO₂ membranes in which CO₂ selectively passes through the membrane. The IEAGHG report describes the membrane process in detail for the following membranes:

- Metallic hydrogen separation membranes
- Porous inorganic hydrogen separation membranes
- Carbon hydrogen separation membranes
- Dual stage hydrogen separation membranes
- CO₂ separation membranes

Tests of various membranes have been conducted using a slipstream of a gasifier fuel gas at the National Carbon Capture Center at Wilsonville. MTR's polymeric CO₂ separation membrane is also being tested at a pilot plant using syngas from a transport gasifier. At the same site, MTP are testing their membrane reactor system at pilot scale. MTR and WPI together are testing their hydrogen membrane.

The IEAGHG paper states that membranes are currently used commercially for CO₂ removal from natural gas at high pressure but development is required before membranes could be used cost effectively on a large scale for pre-combustion capture of CO₂ in power plants. The technology has thus been assessed as TRL-5 in the 2014 report.

94. *Kevin C. O'Brien Ph.D., Gopala, Krishnana Ph.D, Kathryn A. Berchtold Ph.D., Stephan Blum Ph.Dc., Richard Callahand, Will Johnsons, Daryl-Lynn Robertse, Dan Steelea, David Byardf, José Figueroag 'Towards a Pilot-Scale Membrane System for Pre-Combustion CO₂ Separation', a SRI International, Los Alamos National Laboratory, Whitefox Technologies, Visage Energy, BP Alternative Energy International Limited, National Energy Technology Laboratory, 2009*

A multi-organisation and multi-national team from the utility, manufacturing, business and research sectors of the power generation industry was assembled to develop and scale-up a membrane based CO₂ capture system for the pre-combustion capture of carbon dioxide from solid fuels. This next generation system is based on a polybenzimidazole (PBI) membrane originally developed by Los Alamos National Laboratory. Hollow fibres based on a selective layer of PBI onto a porous substrate have been produced. It has been demonstrated that this selective layer can be placed on either the outside (shell side) or inside (lumen side) of the fibre. An Aspen Process simulation was constructed and benchmarked against the literature. There are a number of commercial companies invested in progressing this technology.

95. *Abanades et al., "Emerging CO₂ Capture Systems", International Journal of Greenhouse Gas Control, May 2015*

This paper contains good background on how membranes work, but states that most membrane work has focused on post-combustion CO₂ applications. It recommends that the greatest opportunities for advancement of this technology are to undertake more laboratory and field testing work to understand how each of the membrane types perform on real gas mixtures rather than pure and lab-synthesised streams.

3.3.2 Petrobras Santos Basin Project – Hollow Fibre Membranes

96. *Global CCS Institute: <https://www.globalccsinstitute.com/projects/petrobras-santos-basin-pre-salt-oil-field-ccs-project>
http://www.ieaghg.org/docs/General_Docs/Reports/2016-TR2.pdf*

This natural gas treating with CO₂-EOR project captures approximately 1 MPTA of CO₂. The CO₂ technology is stated to be membrane based using spiral wound and hollow fibre membranes



located on floating production, storage and offloading units with direct injection of CO₂ back into the reservoirs.

Hollow fibre membranes and spiral wound membranes were originally developed for reverse osmosis water treatment applications and have been used extensively, although the Santos Basin project is the only known use for large scale CO₂ separation from natural gas. Since membranes function on a molecular size rather than targeted absorption of the CO₂ molecule, membranes which work for CO₂ removal from methane would not necessarily be applicable for CO₂ removal from syngas.

3.4 Solid Sorbents

3.4.1 Pressure Swing Adsorption

Pressure swing adsorption (PSA) is widely used to separate carbon dioxide, carbon monoxide, methane and water from syngas streams to produce high-purity hydrogen in refineries and petrochemical facilities. The process utilises solid adsorption materials which allow hydrogen to pass through, while trapping all larger molecules at elevated pressures. The bed is then taken offline and the CO₂ rich tail gas is released when the operating pressure is lowered. Several adsorption beds are arranged in parallel with cyclical adsorption / desorption to allow for continuous production of hydrogen.

PSA systems have been in operation for hydrogen production for over 50 years and the technology is considered to be at TRL-9. A range of suppliers offering PSA systems or adsorbents includes:

- Air Liquide
- Air Products
- Linde
- UOP

Pressure swing adsorption is also used to remove carbon dioxide from landfill gas streams, to generate high-purity methane streams suitable for natural gas distribution systems.

97. *Tobias Keller (Linde Engineering), Goutam Shahani (Shure-Line Construction), 'PSA Technology: Beyond Hydrogen Purification', Chemical Engineering, January 2016*

This article provides an uncomplicated summary of the principles and applications for PSA systems in hydrogen purification.

3.4.2 Vacuum Swing Adsorption

98. https://sequestration.mit.edu/tools/projects/port_arthur.html

The Port Arthur Carbon Capture and Storage project is made up of an alliance of Air Products and Chemicals Inc., Denbury Onshore LLC, University of Texas Bureau of Economic Geology, and Valero Energy Corporation. The DOE awarded the Port Arthur project \$900,000 from the American Recovery and Reinvestment Act (ARRA) in October 2009. The project also received an additional \$253 million from the ARRA as part of the DOE's CCS Program Phase 2 in June 2010. This money is matched by \$368 million in private funding.

The project is made up of two post-combustion vacuum swing adsorption units installed downstream of existing Steam Methane Reformers located within Valero's Port Arthur Refinery. The first plant started operations in December 2012, while the second plant began carbon capture operations in March 2013. In June 2016, Air Products announced that it had successfully captured more than three million metric tons of CO₂ within 3.5 years of operation.



CO₂ is captured, dried and purified to 97% purity. It is then delivered via a 12-mile connector pipeline to Denbury's Green Pipeline. Denbury uses the CO₂ for enhanced oil recovery in its onshore operations, with the aim of recovering 1.6-3.1 million additional barrels per year of oil.

The MIT site erroneously describes the Port Arthur project as post-combustion CCS. However, the reference below clearly shows that the CO₂ is removed via VPSA from the syngas stream upstream of the existing, conventional PSA.

99. *John Palamara, Galip Guvelioglu, Steven Carney, 'Air Products: Success in Advanced Separation and CO₂ Processing for EOR: Presented at the 19th Annual CO₂ Flooding Conference', Air Products and Chemicals, Inc., 2013*

This presentation has a simplified block flow diagram of the Port Arthur vacuum swing adsorption process for CO₂ separation on slide 9 and 10.

Since the Port Arthur system is clearly an operating plant at full scale, Wood considers that this technology has reached at least TRL-8.

3.5 Physical Separation

100. *IEAGHG 'Assessment of Emerging CO₂ Capture Technologies and their Potential to Reduce Costs', December 2014*

CO₂ can be separated from syngas by reducing the temperature, resulting in the liquefaction of the CO₂. The temperature involved in this process is typically around -60°C. The cooling can be provided by expansion of the process gas or by external refrigeration. A disadvantage of the process is that to achieve a 90% CO₂ capture rate requires high pressure, in excess of 10 MPa. However, the flip side is that a liquid CO₂ stream is produced which can be pumped at high pressures, thereby avoiding most of the energy consumption and cost of CO₂ compression.

Low temperature separation in general is a well-established technology, using mostly conventional equipment. To date, the processes for low temperature separation are all at the stage of proposals for process line-ups using mainly conventional refrigeration and heat exchange equipment. The technology readiness level was assessed by IEAGHG as TRL-2.

101. *Allan Hart and Nimalan Gnanendran 'Cryogenic CO₂ Capture in Natural Gas', Cool Energy Ltd, 2009*

This paper shares recent field experience and test results from Cool Energy's CryoCell® demonstration plant in Western Australia. The CryoCell® process was developed by Cool Energy Ltd and tested in collaboration with other industrial partners including Shell Global Solutions.

Pure CO₂ has a sublimation point of -78°C compared to the melting point of -182°C for methane, which is the major constituent of natural gas. A natural gas mixture consisting of light hydrocarbons and CO₂ will 'split' into vapour, liquid and solid phases when subjected to thermodynamic equilibrium at certain pressure and temperature conditions. The solid phase produced will be pure CO₂, while the liquid and vapour phases will consist of both CO₂ and hydrocarbons.

The vapour mixture at intermediate pressure and ambient temperature is cooled to a temperature just above the CO₂ freeze point whereby some or all of the stream condenses to a liquid phase. The liquid is then flashed across a Joule-Thomson valve, creating an isenthalpic flash, such that the fluid is split into vapour, liquid and solid. From a process point of view, the pre-cooling temperature and the isenthalpic flash pressure are selected such that the vapour phase CO₂ composition is minimal and the liquid phase methane composition is minimal. The physical separation of the light phase and the dense phase are achieved in a separator vessel, such that the vapour phase has sufficiently low CO₂ to be suitable for export while the dense phase is rich in CO₂ and can be sent for disposal. The solid CO₂ collected in the bottom of the vessel is melted, using an external heat source, such that it mixes with the liquid phase to be removed from the vessel.



As part of commercialising the CryoCell® technology, a demonstration plant was designed and built by Cool Energy Ltd in the Perth basin, Western Australia. The field test programme has demonstrated the technical viability of solid phase CO₂ separation and cost comparison studies indicate improved economic viability for high CO₂ gas field developments. Compared to amine carbon capture technology CryoCell® has the following advantages:

- No process makeup water supply and treatment are required;
- No process heating system required;
- No chemicals are required by the process, hence no consumable costs;
- Water is removed immediately downstream of the inlet separator so there is no corrosion potential and associated corrosion monitoring and mitigation costs;
- No winterisation requirement for cold climates;
- No foaming potential.

However, some of the operating cost savings will be offset by higher rotating equipment maintenance costs for a CryoCell® plant. Cool Energy was hoping to undertake the first commercial application of this new technology soon after publication and had completed the first phase of a FEED study for DrillSearch Energy Ltd for a 60 MMscfd CryoCell® plant with geological storage of CO₂ in the Cooper Basin, in South Australia.

3.5.1 Exxon Mobil Controlled Freeze Zone Technology

Low temperature separation of CO₂ from natural gas is tested and offered commercially, but does not yet have a commercial scale reference. Hence, Wood judges its TRL level to be TRL-7.

102. *Global Carbon Capture and Storage Institute Ltd 2016, 'The Global Status of CCS 2016: Volume 3 CCS Technologies', 2016*

This is the most recent GCCSI global status report. It includes an ExxonMobil case study using Controlled Freeze Zone™ (CFZ™) Technology. This is a single-step cryogenic separation process that removes CO₂ and hydrogen sulphide (H₂S) from natural gas in a specially-designed section of a distillation tower, where CO₂ is allowed to freeze in a controlled manner. Next, the CO₂ is melted and further distilled to recover methane.

In 2008, construction started on a Commercial Demonstration Plant (CDP) at the Shute Creek Treatment Facility at LaBarge, Wyoming. After completing construction and commissioning, a formal test program was conducted from March 2012 through to November 2013. The CDP successfully processed a wide range of sour gas feeds (8 - 71% CO₂ and as much as 36% H₂S), producing natural gas that met pipeline specifications (<2% CO₂ and <4 ppm H₂S). The separated CO₂ was produced at high pressure, reducing compression costs. The paper states that the CDP demonstrated the effectiveness of the technology for CO₂ feed concentrations above 20 per cent.

ExxonMobil now commercially offers its Controlled Freeze Zone technology, following demonstration at Shute Creek Gas Processing Facility.

103. *Global CCS Institute; "Shute Creek Processing Facility"*
<https://www.globalccsinstitute.com/projects/shute-creek-gas-processing-facility>

This useful web database includes mention of ExxonMobil's test programme for the Controlled Freeze Zone Technology.

104. *ExxonMobil; "Controlled Freeze Zone Technology"*,
<http://corporate.exxonmobil.com/en/technology/carbon-capture-and-storage/controlled-freeze-zone/controlled-freeze-zone-technology>

This webpage includes an overview of the Controlled Freeze Zone technology and states that it is now commercially offered by ExxonMobil although this technology does not yet have any commercial references.



3.5.2 Timmins CCS

105. IEAGHG 'Assessment of Emerging CO₂ Capture Technologies and their Potential to Reduce Costs', December 2014

Timmins have proposed a variant to pure low temperature separations. In this process, a recycle loop of the syngas is created and CO₂ levels are allowed to build up so that CO₂ can be removed as a liquid by light refrigeration. This has the advantage of greatly reducing the energy required to compress the CO₂ to export conditions.

The syngas is first used to strip CO₂ from rich Selexol at a temperature of around 70°C. The CO₂ enriched syngas is then circulated through a pre-processing unit to remove water and then a refrigeration unit where part of the CO₂ is condensed and pumped away for export. The syngas with the remaining CO₂ is contacted with the lean solvent in an absorber running at around 20°C. This temperature difference is enough to ensure that the rest of the CO₂ is substantially removed from the syngas for recycling. The net effect is to create a gas loop with a high CO₂ partial pressure which facilitates the liquefaction of the net CO₂ production with light refrigeration, which Timmins claim provides substantial energy savings. The IEAGHG report claims that an independent assessment is in agreement with Timmins claims.

The IEAGHG report highlights some potential issues with the heat recovery network and the solubility of carbon monoxide in the Selexol, which need to be addressed.

Wood judges that the TRL level of low temperature CO₂ separation from syngas to remain at TRL-2 at this time, due to lack of evidence of further practical developments.



4 Oxy-Combustion

4.1 Overview

Oxy-combustion capture refers generally to capture of carbon dioxide using processes in which the combustion oxidant stream is oxygen rather than air, thus removing the large volume of nitrogen present in post-combustion technologies. Oxy-combustion capture initially only referred to schemes in which a conventional boiler was sealed to air ingress and fed with oxygen and recycled flue gas instead of air with associated downstream purification processes. However, in recent years, gas turbine schemes have also been developed which can operate in an oxygen / flue gas oxidant regime, and these are also included under the heading of oxy-combustion.

The 2014 IEAGHG report has given each of the pre-combustion capture technologies researched in this literature review a Technology Readiness Level (TRL). Further development has been conducted for many of these technologies since that time. The following table summarises TRL's given to each technology by the IEAGHG in 2014 alongside the 2017 TRL estimated by Wood resulting from this analysis.

Table 4-1: TRL for Oxy-Combustion Capture Technologies

Technology	2014 TRL	2017 TRL
Oxy-fired Circulating Fluid Bed Boiler (coal)	7	7
Oxy-fired Pulverised Coal Boiler	7	7
Oxy-combustion Flue Gas Purification Units	5-6	5-6
Oxy-fired Gas Turbine Cycles (Allam Cycle)	2	7
Oxy-fired Gas Turbine Cycles (CES Cycle)	5	5
Oxy-fired Gas Turbine Cycles (Others)	2	2

4.2 Oxy-Fired Boilers

The IEAGHG 2014 report states that oxy-fired Circulating Fluidised Bed (CFB) and Pulverised Coal (PC) boilers are sufficiently mature for the next stage to be a full scale demonstration, thus both of these are concluded to have a TRL level of 7. FEED work has been undertaken both for the Oxy-PC case on the White Rose project and for the Oxy-CFB case, for the Compostilla OxyCFB300 project in Spain, but neither of these progressed to detailed design. Further development work has also been undertaken in various aspects of the scheme design and operation, as described in the reference below.

106. Stanger et al., 'Oxyfuel combustion for CO₂ capture in power plants', International Journal of Greenhouse Gas Control, August 2015

This very detailed review paper presents an overview of the developments in oxy-combustion that have occurred in the last ten years, including findings from the larger scale pilots, particularly highlighting the individual areas which have been worked on for each scheme.

The paper mentions the key large pilot plants as:

- Total's Lacq pilot plant in France consisting of a 30 MWth oxy-firing of a natural gas fired boiler storing CO₂ in a depleted natural gas reservoir;
- Vattenfall's Schwarze Pumpe pilot plant in Germany was a 30 MWth Oxy-PC boiler;
- CIUDEN's Technology Development Centre, consists of a 20 MWth Oxy-PC boiler and a 30MWth pilot Oxy-CFB;
- COSPL's Callide Oxyfuel Project in Australia, consisting of retrofit oxy-firing to a 30 MWe coal fired power plant unit.



Also mentioned is a summary of the key full scale demonstration plants which have completed FEED, but since been placed on hold or cancelled.

- Vattenfall's Janschwalde Project;
- CIUDEN and Endesa's Compostilla OxyCFB300;
- KEPCO's Young Dong Project;
- FutureGen 2.0 Project;
- White Rose Project.

Since no full scale demonstrations plants have yet been built, Wood judges that oxy-fired boiler technologies remain at TRL-7.

4.3 CO₂ Purification Units

CO₂ purification units are often divided into stages, such as the "warm section" and the "cold section", or as "flue gas section" and "CO₂ purification section". In general, removal of particulates, NO_x and SO_x components will be required as well as mercury, hydrogen chloride and final separation of water and inerts, such as argon and nitrogen. The most challenging separation can sometimes be achieving the oxygen removal specification, with a limit of 100 ppmv being common to many projects.

The IEAGHG 2014 TR4 report and the review paper by Stanger et al include information on the development of CO₂ purification units for oxy-combustion CO₂ capture plants.

CO₂ Purification Units, of sorts, have been included at the main large oxy-combustion pilot plants as follows:

- The Schwarze Pumpe demonstration facility included CO₂ liquefaction, and NO_x and SO_x removal technologies as well as Air Product's Sour Compression scheme and Linde's LICONOX process;
- At the Lacq site the CPU consisted of a CO₂ compressor and a dehydration unit;
- At CIUDEN's Oxy-CFB plant the CPU consisted of a flue gas filter, compressor, dehydration unit and cold box provided by Air Liquide;
- Callide's CPU consists of a compressor, but no further details are mentioned.

The Air Products sour compression system incorporates removal of NO_x and SO_x into their respective acids in contacting columns and is based on a technology they have been developing and had variants under patent for more than 10 years.

The Linde LICONOX process uses a flue gas desulphurisation stage to remove SO_x followed by an ammonia wash to remove NO_x, as well as a cold box.

Praxair proposes two options for CPU schemes, the first based on a sulphuric acid wash and the second using activated carbon.

Air Liquide propose a process using NaCO₃ quench to remove SO_x with NO_x removal at the knock out drum of the CO₂ compressor, with final removal in a separate distillation column in the cold box.

The IEAGHG 2014 report gives the TRL level of the Linde and Air Liquide processes as TRL-7 and the Air Products and Praxair systems as TRL-6. It is Wood's judgement that since no larger plants have been operated since these findings, the TRL levels remain unchanged.



4.4 Oxy-fired Gas Cycles

107. IEAGHG, 'Oxy-Combustion Turbine Power Plants', 2015/05, August 2015

The IEAGHG report on oxy-combustion turbine power plants looks at a number of most relevant systems featuring oxy-turbine cycles. The types of technologies discussed in the report are:

- Semi-closed oxy-combustion combined cycle (SCOC-CC);
- MATAINT cycles;
- NET Power cycle;
- Graz cycle;
- CES cycle;
- AZEP cycle;
- ZEITMOP cycle.

These can be grouped into three generic processes. The SCOC-CC, MATAINT and NET Power cycles use CO₂ as a major component of the working fluid mixture. Carbon dioxide is cooled and recycled back from the exhaust to the combustor inlet, acting as a temperature moderator, i.e. preventing the temperature of the combustor from rising too high. The Graz and CES cycles use steam as a major component of the working fluid mixture and also as a temperature moderator for the combustor.

The AZEP and ZEITMOP cycles use high temperature membrane technology, which separates O₂ from the hot pressurised air stream. The externally heated air cycle is used as the main power cycle for the AZEP cycle, whereas for ZEITMOP it is used as a side cycle to the principal CO₂ cycle.

Based on the technology development and efficiencies found in the literature review, the IEAGHG study analysed the following four cycles in detail for its techno-economic assessment:

- Semi-closed oxy-combustion combined cycle (SCOC-CC);
- Graz cycle;
- CES cycle;
- NET Power cycle.

4.4.1 SCOC-CC Cycle

The process is similar to a conventional combined cycle except that the inlet gas to the Gas Turbine compressor is recycled CO₂-rich gas rather than air. Oxygen from the ASU is fed directly to the combustor. The exhaust gas passes through the HRSG system to produce steam. The cooled gas from the HRSG is further cooled to condense out water, leaving a CO₂-rich gas. Most of the cooled CO₂-rich gas is recycled back to the compressor and the rest is compressed and purified for transportation and storage.

SCOC-CC has been proposed and studied by various organisations. In the literature, the net efficiency of the gas fired SCOC-CC based power plant is reported in the range of 45-48% using a pressure ratio of 30-45 bara and firing temperature of ~1300°C.

Even though it is the simplest form of the oxy-combustion cycle, with similar features to a conventional combined cycle, the unusual working fluid in the gas turbine cycle turbo-machinery of the SOCC-CC plant needs to be developed from first principles, requiring huge investment for the R&D efforts.

4.4.2 Graz Cycle

The system consists of a high temperature cycle and a low temperature steam cycle. The high temperature cycle consists of the gas turbine, HRSG, compressor and a high pressure steam



turbine. The steam generated in the HRSG and the recycle water-CO₂ mix gas are used to cool the burners and the turbine blades.

The Graz cycle has been studied by various institutes and has been modified to improve the efficiency. The predicted net efficiency has been reported as 48.6%. Particular attention has been given to the development of the turbo-machinery, especially the high temperature turbine, which requires a completely new design. Another important issue is related to the use of H₂O-rich stream being used for turbine blade cooling. Overall, the cycle is still immature and needs to be developed further.

4.4.3 CES Cycle

This cycle, proposed by Clean Energy Systems, uses water both in liquid and vapour phases as combustion temperature moderator. It has been reported that a dedicated turbine design with an inlet temperature of ~1700°C can theoretically achieve a net efficiency of ~50% for a 400 MWe plant. The performance has been reviewed and studied by others. Kvamsdal et al (2007) predicted a net efficiency of ~45%. It is difficult to justify such variable results.

CES has developed a test facility in Kimberlina, California. A conventional gas turbine has been adopted for the high temperature turbine (modified GE J79) and the modified Siemens steam turbine SST-900 was used. Information related to the performance is not available in the public domain. For the commercial plant, a dedicated design is needed for the high temperature, high pressure system dealing with supercritical steam and liquid water for the temperature moderator.

108. CES press release, "CES is conducting a feasibility study into the development and deployment of carbon negative "BIOCCS" power plants"

The above announcement on the CES website indicates that it is undertaking a feasibility study into using biomass derived syngas in its own oxy-fuel Gas Generator followed by its gas cycle to produce carbon negative power and that it plans to deploy a small scale commercial demonstration "BioCCS" plant at the Kimberlina Facility.

4.4.4 NET Power Cycle

In the report, the NET Power technology contains the latest and most complete information. Detailed modelling and cost data is presented for the NET Power cycle. Most importantly, the IEAGHG results for NET Power have been checked and commented on by the technology developer. The NET Power cycle also has the highest efficiency out of all the cycles reviewed for the report. The IEAGHG report has calculated an efficiency of 55% for NET Power whereas the developers have estimated an efficiency of 59% for their cycle using proprietary knowhow and improvements.

Considering that a 50 MWth demonstration plant is undergoing commissioning at this time, Wood judges the TRL level of the Net Power system to be TRL-7.

109. Allam, John Rodney, et al. "System and Method for High Efficiency Power Generation Using a Carbon Dioxide Circulating Working Fluid", Palmer Labs, LLC, assignee. Patent 2013/0213049 A1. 22 Aug 2013.

In the patent, an example of the NET Power system is described using pure methane as fuel (page 45). The example models the NET Power system to produce 1 lbmol of CO₂ product from methane fuel with all key stream temperatures, pressures, flow splits and recycles being specified. This is the example that was modelled by Wood for the IEAGHG study using Aspen Hysys to try to match the NET Power cycle. This model has been modified for natural gas fuel to see the effect of natural gas combustion on different process parameters, contaminants and recycles.

110. Allam, John Rodney "NET Power's CO₂ cycle: the breakthrough that CCS needs", Modern Power Systems, 10 July 2013.

This paper describes the proprietary NET Power cycle utilising CO₂ as the working fluid in a high-pressure, low-pressure ratio, single turbine. The cycle includes a high pressure oxy-fuel combustor



that burns natural gas in a pure oxygen stream to provide a high pressure feed stream to a power turbine.

Figure 3 in the report is very useful to understand the thermodynamic behaviour of CO₂ as its phase changes and how this affects the energy balance of the system. The imbalance between the heat liberated by the low-pressure turbine exhaust and the heat required to raise the temperature of the high-pressure recycle flow from its lowest temperature point is apparent. This imbalance is caused by a very large increase in the specific heat of CO₂ in the high-pressure recycle flow at the low-temperature end of the economiser heat exchanger.

The NET Power cycle addresses this issue at the low-temperature end of the heat exchanger by incorporating waste heat generated by the air compressors of the cryogenic air separation plant into the CO₂ flow.

111. *Allam, John Rodney, et al. "High Efficiency and Low Cost of Electricity Generation from Fossil Fuels while Eliminating Atmospheric Emissions, Including Carbon Dioxide", GHGT-11, Energy Procedia 37 (2013) 1135 – 1149.*

This GHGT-11 paper describes the proprietary NET Power cycle utilising CO₂ as the working fluid in a high-pressure, low-pressure ratio Brayton cycle, operating with a single turbine that has an inlet pressure in the range of 200 bar to 400 bar and a pressure ratio of 6 to 12.

The paper provides information on how adiabatic heat of compression from the ASU can be transferred to the CO₂ recycle stream using a closed cycle heat transfer fluid.

The only notable difference between this publication and others is the oxygen compression system. This paper suggests that the cryogenic air separation system can be designed to produce oxygen at pressures between 30 bar and 80 bar so that it can be blended with CO₂ streams from the suction, inter-stage, or delivery of the CO₂ compressor. A separate O₂ / CO₂ compressor delivers the oxidant mixture to the combustor at the required high pressure. It is not necessary to produce high pressure oxygen directly from the air separation system at pressures above 200 bar. The oxidant mixture is preheated in the economiser heat exchanger before entering the combustor.

112. *Manso, Ricardo Llorente "CO₂ Capture in Power Plants - Using the Oxy-combustion Principle", Masters' Thesis, Department of Energy and Process Engineering, Norwegian University of Science and Technology, July 2013.*

This is a masters' thesis prepared by Ricardo Llorente Manso of Norwegian University of Science and Technology. The thesis investigates different oxy-combustion cycles both for coal and natural gas fuel including the Allam Cycle of NET Power Technology in order to establish the efficiency potential and operational advantages and drawbacks of different oxy-combustion processes.

The NET Power process has been simulated together with other power plants with pre-combustion and post-combustion capture and without capture for natural gas and coal.

The NET Power cycle model is developed considering the oxygen from the ASU at 75 bar is diluted with a CO₂ stream and compressed to the required high pressure of the combustor using a separate O₂ / CO₂ compressor. The compressed oxidant is then preheated by the turbine exhaust before entering the combustor.

In the thesis, the NET Power cycle is modelled using both pure methane and natural gas as fuel. The technical performance table provides useful information as to how the NET Power system responds to the pure methane and natural gas. The table shows the efficiency drop by switching from methane to natural gas.

The NET Power process simulation using both natural gas and coal give lower efficiencies than that proposed by the technology provider. For natural gas, the simulation predicts an efficiency of 52%, instead of 59% claimed by NET Power.



113. *Allam, John Rodney, et al. "Cryogenic Air Separation Method and System", 8 Rivers Capital LLC, Patent US2012237881— 2012-09-20.*

The invention relates to a cryogenic air separation process design that provides high pressure oxygen for an oxy-fired combustion process and how the air separation process can be directly integrated into a closed cycle power production process utilising a working fluid, such as CO₂. The cryogenic ASU can be integrated into a process to provide an external source of heat by eliminating the need for inter-cooling between air compression stages and provides for recycling the adiabatic heat of compression into the process step, wherein an additional heat supply is beneficial.

114. *R. Allam et al., "Demonstration of the Allam Cycle: An update on the development status of a high efficiency supercritical carbon dioxide power process employing full carbon capture" GHGT-13, November 2016, Lausanne, Switzerland*

This update paper presented to GHGT-13 indicates that the 50 MWth demonstration plant entered the commissioning stage in 4Q2016 and is anticipated to start transferring power to the grid by the end of 2017. Development design work is ongoing such that data from the 50 MWth plant can inform the final design of a proposed 300 MWth plant. The paper also includes a description of the solid fuel fed variant of the flow scheme, which has been developed theoretically with parallel work on four key development hurdles being undertaken in North Dakota. It is intended that a coal demonstration plant could closely follow the 300 MWth gas plant.

115. *Kirchner, Robb "The NET Power Process", International Gas Network Meeting, 31 May 2013. <http://www.apgtf-uk.com/files/workshops/13thWorkshop2013/36RobbKirchner.pdf>*
116. *Isles, Junior "Fossil fueled power generation without CO₂ air emissions", The Energy Industry Times - August 2012.*
117. *Toshiba Signs Agreement "To Develop Next Generation Thermal Power System" with NET Power, Shaw and Exelon, Press Release Toshiba Corporation, June 15, 2012.*
118. *Gibbins, Jon "CCS Technology Development and Deployment: Current Status and Some Potential Developments" UKCCS Research Centre, London, 27 Sept 2013 www.ukccsrc.ac.uk/system/files/.../Jon_Gibbins_GDLon27.9.13.pdf*

These papers have been reviewed, but did not contain any additional relevant information to the sources described above.

4.4.5 Costain Power Cycle

119. <http://www.costain.com/media/596752/gas-carbon-capture-oct15-2pp-size-747kb.pdf>

This is a Costain promotional poster on its carbon capture technology. It has some limited information on their Oxyfuel Penalty Reduction Option Programme (OxyPROP). The technology is a patented low temperature CO₂ separation and compression technology: low temperature processing with close heat integration to capture CO₂. Costain claims that the process has high thermodynamic efficiency, close integration of CO₂ purification with compression train, and no use of process solvents / sorbents or external refrigeration. Costain has developed the basic design together with the University of Edinburgh and University of Leeds, with funding from DECC.

120. http://www.costain.com/media/1065/inp_007_carbon_capture_and_storage_oxyprop.pdf

An oxyfuel power plant involves burning coal in oxygen, rather than in air, resulting in a concentrated stream of CO₂ which is readily captured and purified for storage. Costain has developed a patented approach for CO₂ separation and compression. A process flow diagram is shown in the document.

121. *Carolina Font Palma, 'Oxyfuel Power Plant with Novel CO₂ Separation and Compression Technology', UKCCSRC Biannual Meeting, 3 April 2014*

The slides present the OxyPROP project, and include descriptions of the CPU scheme selection, power plant model, steam cycle model and heat integration, the results and conclusions.



For the project, a steady-state integrated model was used to analyse power plant performance, modelling and penalty reductions for oxyfuel combustion. Increased LHV efficiency and increased CO₂ purity were brought about through a heat integration method and modified low temperature process within the CPU. The highest efficiency was achieved for compression trains with conventional inter-stage temperatures and carefully integrated intercooler / aftercooler duties.



5 Chemical Looping

5.1 Overview

There are a number of technologies which involve the use of solid sorbents and reactants which employ adsorption, absorption and chemical reaction with solids to capture CO₂ from process streams and exhaust gases. For technologies where solid sorbent processes have been applied to post-combustion capture, refer to section 2.4, and for technologies where they have been applied for pre-combustion capture, refer to section 3.4.

In this section, only those technologies which can be classed as chemical looping will be included, as these can often be applied in post-combustion, pre-combustion and oxy-combustion configurations, and are thus considered separately.

The 2014 IEAGHG report has given the technologies researched in this literature review a Technology Readiness Level (TRL). The following table summarises TRL's given to each technology by the IEAGHG in 2014 alongside the 2017 TRL estimated by Wood resulting from review of the literature.

Table 5-1: TRL for Chemical Looping Capture Technologies

Technology	2014 TRL	2017 TRL
Post-Combustion Calcium Looping	6	6-7
Sorbent-Enhanced Water Gas Shift (SEWGS)	5	5
Chemical Looping Combustion	2	6-7
Chemical Looping Combustion with Oxygen Uncoupling	1	2-3
Chemical Looping Steam Reforming	3	3

“Calcium Looping” and “Chemical Looping Combustion (CLC)” refer to CO₂ capture processes which involve capture of CO₂ via chemical reaction with a regenerable solid carrier at high temperature. The carrier is introduced to the oxidation side of the processes, forming a compound including CO₂ (e.g. CaCO₃), which is then moved to a reduction vessel, where the CO₂ is released, regenerating the carrier (e.g. to CaO).

Alternatives to both Calcium Looping and CLC can also be used to produce a hydrogen rich syngas in a pre-combustion CO₂ capture scheme, generally also promoting the water gas shift reaction. These technologies are termed Sorbent-Enhanced Water Gas Shift (SEWGS).

5.2 Calcium Looping

Chemical looping schemes were first discussed as a development of solid sorbent systems in which an adsorbent is employed for post-combustion CO₂ capture using a pair of fluidised beds, with CO₂ being adsorbed in one bed and the adsorbent being regenerated in the other. Chemical looping increases the affinity between adsorbent and CO₂ by introduction of a chemical reaction between the solid material and the CO₂, which is then reversed in the second reactor to regenerate the material. This has therefore been most commonly employed for post-combustion CO₂ capture using calcium as the carrier, in which case the process is referred to as “Calcium Looping” (CaL).

The IEAGHG 2014 TR4 Assessment of Emerging CO₂ Capture Technologies gives a status snapshot of operating calcium looping pilot plants and a sensitivity to a range of key cost parameters and gives calcium looping for post-combustion CO₂ capture a TRL of 6.

Once the LEILEC plant or the Alstom large scale demonstration is in operation, calcium looping technology for post-combustion CO₂ capture will have advanced to TRL-8, but since these are both



still in development, Wood judges that this technology is currently at TRL 6-7, justified by the operation of Alstom's 3 MWth sub-scale demonstration plant.

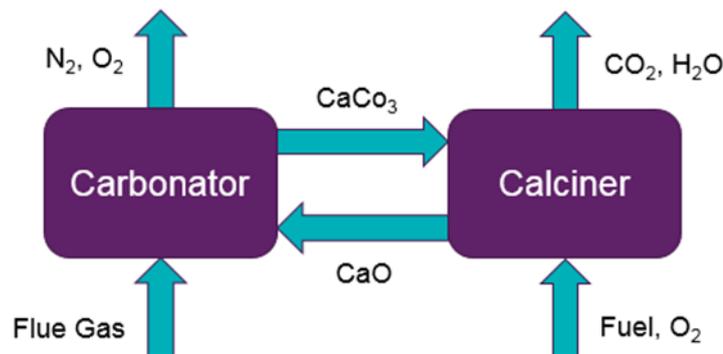


Figure 5-1: Calcium Looping Schematic

A modification of the calcium looping process is described whereby the heat required for calcination is provided indirectly, removing the need for an oxygen feed and an ASU. This process is termed “indirectly heated CaL”.

The benefit of combining CaL with cement production is discussed in the IEAGHG report, although the integration aspects are only given a TRL of 1 in the 2014 report, this should leap forward with the LEILAC plant demonstration (see below).

122. C.C. Dean, J. Blamey, N.H. Florin, M.J. Al-Jeboori, P.S. Fennel, ‘The calcium looping cycle for CO₂ capture from power generation, cement manufacture and hydrogen production’, Imperial College of Science, Technology and Medicine, 2011

This paper describes the calcium looping CO₂ capture scheme using solid CaO-based sorbents to remove CO₂ from flue gas, e.g. from a power plant, producing a concentrated stream of CO₂ (~95%) suitable for storage.

The Ca-looping process is described as exploiting the reversible gas-solid reaction between CO₂ and CaO(s) to form CaCO₃(s). Calcium looping has a number of advantages compared to closer-to-market capture schemes, including: the use of circulating fluidised bed reactors; sorbent derived from cheap, abundant and environmentally benign limestone and dolomite precursors; and the relatively small efficiency penalty that it imposes on the power / industrial process (estimated at 6 - 8 percentage points, compared to 9.5 - 12.5 from amine-based post-combustion capture). A further advantage is the synergy with cement manufacture, which potentially allows for decarbonisation of both cement manufacture and power production. In addition, a number of advanced applications offer the potential for significant cost reductions in the production of hydrogen from fossil fuels coupled with CO₂ capture. A range of applications of calcium looping are discussed in the paper.

The paper states that several independent projects have been initiated in order to scale-up Ca-looping technology, including pilot plant trials (up to ~120 kWth) with CO₂ capture in the USA, Canada and Spain. In addition, larger scale demonstrations are planned (~2 MWth). To the date of publication, those projects had demonstrated good levels of CO₂ capture efficiency (~ 80 - 90%), identifying that future work needing to focus on process efficiency and generating a CO₂ stream suitable for storage.

123. Adina Bosoaga, Ondrej Masek, John E. Oakey, ‘CO₂ Capture Technologies for Cement Industry’, Mott MacDonald, Energy Technology Centre Cranfield University, 2009

This paper summarises the different CO₂ capture technologies suitable for the cement industry and assesses the potential of the calcium looping cycle as a new route for CO₂ capture in the cement industry.

The potential advantage of this system is described as the very low efficiency penalty expected (<6%) compared with other capture technologies. Since limestone is already used for cement manufacture, and because it is a cheap material with good geographical distribution, it allows the use of local limestone resources with minimal limestone related infrastructure investment.

Another envisaged benefit of this technology is that the lime purged from the cycle could be used as a raw material for the production of cement clinker. Therefore, the calcium looping cycle is described as potentially having an important impact in reducing CO₂ emissions from the cement industry, and is also applicable in other sectors, such as carbon capture from power plants.

5.2.1 Calix Calcium Looping Technology

124. Adam Vincent, Daniel Rennie, Mark Sceats, Matthew Gill, Simon Thomsen, 'Public LEILAC pre- FEED Summary Report', Project LEILAC, October 2016

This report describes the LEILAC project (Low Emissions Intensity Lime And Cement). Its aims are to successfully pilot a breakthrough technology that aims to replace an existing part of the cement and lime making process and enable the capture of unavoidable process CO₂ emissions without significant energy penalty at comparable capital costs to conventional equipment.

This project is primarily based on the development and testing of a suitably sized pilot plant to validate the technology and facilitate scale-up. The project will develop, build, operate and test a 240 TPD pilot plant at Heidelberg Cement's plant in Lixhe, Belgium, with the aim of demonstrating capture of over 95% of the process CO₂ emissions. The process is demonstrated at commercial scale for processing magnesite, however, applying this technology to a cement or lime plant requires research, development and careful engineering, as these materials need to be calcined at much higher temperature and scale.

The consortium members included the technology provider; Calix, Heidelberg Cement, CEMEX, Tarmac, Lhoist, Amec Foster Wheeler, ECN, Imperial College, PSE, Quantis and the Carbon Trust. It is supported by CEMBUREAU, ECRA, and EuLA. Funding for the project has been provided by the consortium members (€9M) and the European Commission through the Horizon 2020 research and innovation programme (€12M, grant no. 654465).

Calix describe the equipment involved as a reversing axial separator (RAS) technology previously demonstrated on the CFC850 DSR pilot in Bacchus Marsh, Australia. The design maintains centrosymmetric geometry, minimising stress on the reactor. In this case, the process CO₂ stream, released by the calcined material, is separated from the powder by reversing the direction of flow at the bottom of the reactor. The gas and a small percentage of solids travel up a central internal tube, exiting the top of reactor where it is filtered. The calcined solids exit from the bottom of the reactor. Results from trials of the system indicated a design can be achieved that should enable the required separation efficiency of the CO₂ and powder.

125. Thomas P. Hills, Mark Sceats, Daniel Rennie, Paul Fennell, 'LEILAC: Low Cost CO₂ Capture for the Cement and Lime Industries: 13th International Conference on Greenhouse Gas Control Technologies, GHGT-13, 14-18 November 2016, Lausanne, Switzerland', Imperial College London, Calix Europe Limited, 2017

This paper further describes the LEILAC concept and gives an update on the status of the development. The project is going through the front end engineering design process and is planned to begin operation during 2019.

5.2.2 Alstom Calcium Looping Technology

126. Corinne Beala, Eric Bouqueta, Herbert E. Andrus, Jr.b, Carl Edbergb , Iqbal Abdullally, 'ALSTOM Chemical Looping Technology Status', ALSTOM Power Boilers, IEAGHG Oxyfuel Combustion Conference 2, Energy Procedia, 2011.

In this paper, Alstom's development programme for chemical looping is described, including two separate technologies under development; one using calcium oxides and another using metal oxides (see section 5.4.1).



The calcium oxides (CaOx) project is funded partly by Alstom and partly by the US DOE. It uses a cold flow model and involves validation of a 3 MWth scale design under autothermal operation.

Both prototypes have been built and operated, confirming both the chemistry involved and the solid transport mechanics.

127. *F. Kluger, H. Andrus, I. Abdulally, A. Levasseur, C. Beal, J. Marion, 'Overview of ALSTOM's Chemical Looping Programs', 5th Meeting of the IEAGHG Oxyfuel Combustion Research Network, Wuhan, China, October 2015.*

In this presentation, the two processes involved in the two parallel areas of development are described, along with some results from running the 3 MWth pilot described above.

128. *A. Levasseur, J. Marion & F. Vitse, 'ALSTOM's (GE) Chemical Looping Combustion Technology with CO₂ Capture for New & Existing Coal-Fired Power Plants (FE0009484), 2016 NETL CO₂ Capture Technology Meeting, Pittsburgh, PA, August 2016*

This presentation describes the limestone based looping programme with more detail around the chemistry. Since the older publications, the 3 MWth prototype has been relocated to Bloomfield, CT, a new 100 kWth chemical looping facility has been completed and six 100 kWth test programs have been completed to address technical gaps. The conclusion of the presentation is that development is continuing and further 100 kWth tests are planned to address remaining technical gaps. It is claimed that GE is still on target to validate the process and move towards a large scale demonstration.

5.2.3 Origen Power Technology

129. *Innovate UK Innovation Showcase, Department of Energy & Climate Change, Slides: 144-160, 2016*

This presentation describes Origen Power's process which uses natural gas to generate electricity whilst removing carbon dioxide from the atmosphere, using a fuel cell and calciner. Details of the anticipated performance and benefits of the process are not entirely clear from the published material. However, a process flow diagram is given on page 155. This process is not strictly calcium looping, as the generated lime appears to be produced continuously from fresh limestone feed and not recarbonated within the process.

5.3 Sorbent-Enhanced Water Gas Shift (SEWGS)

130. *IEAGHG 'Assessment of Emerging CO₂ Capture Technologies and their Potential to Reduce Costs', 2014/TR4, December 2014*

A range of CaL processes for CO₂ capture from hydrogen production are presented in the above report including combined shift-carbonation whereby the equilibrium shift reaction is aided by the removal of CO₂ from the gas phase into the solid phase.

The initial concept, called Sorbent-Enhanced Water Gas Shift (SEWGS), used a packed bed containing a mixture of a steam methane reforming or water gas shift conversion catalyst and a selective adsorbent which removes the CO₂ from the high temperature reaction zone, thus driving the reaction to completion. The adsorbent is then periodically regenerated using PSA or TSA methods.

SEWGS has been developed at the laboratory scale in the EU FP7 project CAESAR. The next stage of the process development will be pilot testing with coal based syngas to prove the long term stability of the sorbents. The IEAGHG report states that this technology is assessed as TRL-5.

Since an ECN pilot plant is under construction, Wood agrees with the IEAGHG assessment of TRL-5, but it will hopefully move to TRL-6 soon, once the pilot plant is running.

131. *STEPWISE Project: <http://www.stepwise.eu/project/>*



The main objective of the proposed STEPWISE project is to scale up the SEWGS technology for the CO₂ capture from Blast Furnace Gas. The STEPWISE project aims to construct and operate a SEWGS pilot test installation at a blast furnace site. They have six work packages, with the final work package to have full scale design, costing, business case and business plan achieved.

132. STEPWISE Pilot of SEWGS Technology at Swerea/Mefos:

<https://www.globalccsinstitute.com/projects/stepwise-pilot-sewgs-technology-swereamefos>

The pilot unit is designed, being built and will be operated by Swerea Mefos in close collaboration with ECN. The physical adsorption SEWGS reaction technology will be tested on blast furnace gas from the nearby steel plant of SSAB. The capture capacity of the pilot plant is 14 TPD of CO₂.

The SEWGS process was initially developed as a pre-combustion technology but can be also applied to blast furnace gas. The process combines three processes in one reactor system:

- CO₂ adsorption;
- simultaneous acid gas removal (H₂S, COS);
- the water-gas shift (WGS) reaction.

In conventional CO₂ removal technologies, the CO conversion to CO₂ within the WGS section dictates the capture ratio of the downstream separation. High CO conversion is required to reach a high CO₂ capture ratio, at the expense of significant steam addition to the WGS section. By contrast, the SEWGS process can yield potential steam savings and allows the use of novel catalysts and process schemes. WGS improvements to be tested in the pilot are:

- use of novel catalysts with lower steam demand;
- novel reactor arrangement in split flow configuration.

Both improvements aim at minimising the steam requirement for the overall CO₂ separation and involve both catalyst and process development and demonstration.

SEWGS is a multi-column reactive hot Pressure Swing Adsorption (PSA) process. In the pilot, however, a single column is used to demonstrate the H₂-CO₂ separation. The single column contains about 2.5 tonne of sorbent material and is operated in counter-current pressure-swing mode. Operation of the pilot will focus on the steam requirement to obtain the targeted separation efficiency, cycle design, heat management and the interplay between the WGS and the SEWGS sections. The data will serve as reference to fine-tune the SEWGS simulation model.

ECN (Netherlands) is providing the SEWGS technology. The pilot plant is being built at and will be operated by Swerea MEFOS (Sweden). The Politecnico de Milano (Italy) and the Universitatea Babeş-Bolyai (Romania) will undertake the techno-economic and life-cycle analyses of the SEWGS based technology with alternative CO₂ capture technologies. SSAB and Tata Steel Consulting (United Kingdom) support the project with their understanding of the processes involved in modern integrated steel plants.

5.3.1 Calix ENDEX SEWGS Technology

133. Calix Endex Reactor Carbon Capture Technology Feasibility Study, 2012

Innovate UK funded Calix to perform a feasibility study on its ENDEX reactor in 2012. The summary of the project states that Calix is developing a technology for carbon capture from syngas. Calix describes its technology as a new approach that is based on calcium looping, but applied to pre-combustion capture in order to shift and decarbonise syngas rapidly at high temperature and pressure. The process is described as unique because it has no primary energy penalty and compared to post-combustion schemes, the higher pressure operation is said to keep the equipment small and the costs low. The performance target is for a full scale combined cycle power plant with CCS to have an efficiency of >50%. Compared to existing calcium looping, the Calix process retains the heat flux within the reactor and uses light carbonation to eliminate sintering.



134. Patent: <https://www.google.com/patents/US8449853>

This patent describes the ENDEX Configuration and was filed by Calix Limited.

135. Paul Fennell and Ben Anthony, 'Calcium and Chemical Looping Technology for Power Generation and Carbon Dioxide (CO₂) Capture, Woodhead Publishing Series in Energy: Number 82, 2015

This book has a chapter on Calcium Looping by pressure-swing and the ENDEX concept. The chapter describes that many of the applications of chemical looping for reforming and gasification have considered temperature-swing Calcium Looping. However, calcination / carbonation can also be achieved by CO₂ partial pressure-swing, which is the approach taken with Calix's ENDEX (endothermic-exothermic) reactor technology concept. Calcination requires lower temperatures than carbonation, therefore to drive the endothermic calcination reaction and take advantage of the heat transfer between the carbonator and calciner the carbonator pressure is elevated and the calciner is operated at atmospheric pressure.

The condition of an elevated inlet gas stream to the carbonator makes pressure swing chemical looping most applicable for integration with reforming and gasification applications, including pre-combustion capture from the NGCC plant, for syngas from an IGCC plant, or for natural gas treating.

The chapter discusses Calix Limited and Millennium Generation Ltd plans to demonstrate the Endex Reactor Technology for producing H₂-rich fuel gas from natural gas with CO₂ capture.

136. <http://www.our-future.co.uk/millennium-generation/latest-news/post.php?s=2015-07-02-millennium-generation-ltd-completes-front-end-engineering-design-feed-for-2mw-endex-demonstration-facility>

In July 2015, Millennium Generation, a joint venture with Calix, announced that it had completed a front end engineering design (FEED) for a 2 MWth ENDEX demonstration facility to be located at a site in the Yorkshire / Humberside region of the UK. The demonstration was planned to showcase pre-combustion carbon capture at >85% on fuel gas from reformed natural gas. However, it does not appear that this particular demonstration has progressed past FEED.

5.4 Chemical Looping Combustion

Chemical Looping Combustion (CLC) is an oxy-combustion CO₂ capture technique in which an oxygen carrier supplies oxygen to the fuel reactor then carries CO₂ to the reduction reactor where the CO₂ is recovered. This process means that fuel and air do not mix. Different carriers are used for CLC such as NiO, MgO and CuO.

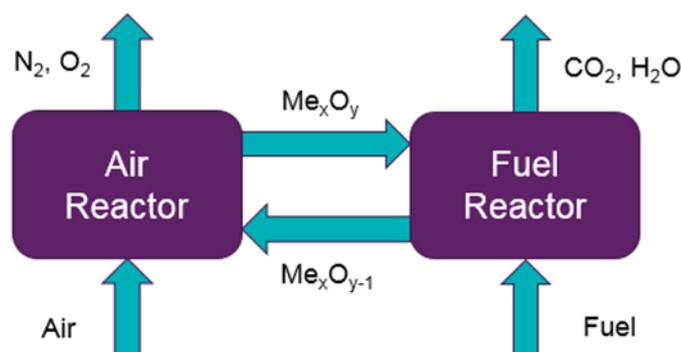


Figure 5-2: Chemical Looping Combustion Schematic

CLC is presented in the IEAGHG report showing a potential for achieving 42% electrical efficiency on coal but with only a TRL of 2 despite large scale tests, including Alstom's 3 MWth pilot discussed below.

Since Alstom seem to have operated their 1 and 3 MWth pilot plants fairly extensively, Wood judges that this technology has now reached TRL 6-7.

137. *Anders Lyngfelt* and Carl Linderholm, "Chemical-Looping Combustion of Solid Fuels – status and recent progress", Department of Energy & Environment, Chalmers University of Technology, GHGT-13, Lausanne, Switzerland, 2016*

This paper states that CLC of solid fuels has been investigated and trialled for 10 years, and summarises the operational experience and progress that has been made in that time. Thus far, more than 70 different materials have been used to pilot CLC schemes with results reported in more than 150 publications. It is stated that more than 3000 operating hours of pilot testing has been achieved under various conditions which show that CLC is technically feasible. It also states, however, that scale up will not be straight forward due to inherent differences between the operation of large and small scale fluidised beds.

5.4.1 Alstom Chemical Looping Technology

138. *Corinne Beala , Eric Bouqueta , Herbert E. Andrus, Jr.b, Carl Edberg , Iqbal Abdulally, 'ALSTOM Chemical Looping Technology Status', ALSTOM Power Boilers, IEAGHG Oxyfuel Combustion Conference 2, Energy Procedia, 2011.*

In this paper Alstom's development programme for chemical looping is described, including two separate technologies under development; one using calcium oxides and another using metal oxides.

The metal oxides (MeOx) project is called ÉCLAIR (Emission free chemical looping coal combustion process) and is partly funded by Alstom and partly funded by the EU under the Coal and Steel research funding budget. This project aimed to validate the process at a 1 MWth scale and achieve autothermal operation.

Both prototypes have been built and operated, confirming both the chemistry involved and the solid transport mechanics.

139. *F. Kluger, H. Andrus, I. Abdulally, A. Levasseur, C. Beal, J. Marion, 'Overview of ALSTOM's Chemical Looping Programs', 5th Meeting of the IEAGHG Oxyfuel Combustion Research Network, Wuhan, China, October 2015.*

In this presentation, the two processes involved in the two parallel areas of development are described, along with some results from running the 1 and 3 MWth pilots described above. It is stated that the ÉCLAIR program has achieved autothermal operation and reached gasification conditions.

Alstom are using a further development of the piloted scheme as a generator of high hydrogen syngas from coal for liquid fuel production and or power generation with CO₂ capture but a specific reference to this technology was not found in the public domain within the timescale of this study.

5.5 Chemical Looping Combustion with Oxygen Uncoupling

It is not clear from the literature if the full system has been validated at bench scale yet, although there has clearly been some significant effort spent on developing the flow scheme. Wood judges that this technology is now at either TRL-2 or 3.

140. *Calin-Cristian Cormos, 'Chemical Looping with Oxygen Uncoupling (CLOU) concepts for high energy efficient power generation with near total fuel decarbonisation', Babeş-Bolyai University, Romania, Applied Thermal Engineering, February 2017*

This paper describes the concept of chemical looping with oxygen uncoupling, which is a variant of the chemical looping process, in which the oxygen carrier releases gas phase oxygen to the fuel combustion side of the process in a distinct step prior to combustion, for example 4CuO becomes 2Cu₂O + O₂ prior to combustion. This additional step is said to be helpful for increasing the fuel



conversion and thus the overall performance of the scheme. In this paper, the scheme is compared with various benchmarks, against which it is stated to show significant advantages.

141. *Amit Bhave, Richard H.S. Taylor, Paul Fennell, William R. Livingston, Nilay Shah, Niall Mac Dowell, John Dennis, Markus Kraft, Mohammed Pourkashanian, Mathieu Insa, Jenny Jones, Nigel Burdett, Ausilio Bauen, Corinne Beal, Andrew Smallbone, Jethro Akroyd, 'Screening and techno-economic assessment of biomass-based power generation with CCS technologies to meet 2050 CO₂ targets', CMCL Innovations, E4tech, Imperial College London, Doosan Power Systems, Department of Chemical Engineering and Biotechnology, University of Cambridge, Faculty of Engineering, University of Leeds, EDF Energy, Drax Power, Alstom Boiler France, Nanyang Technological University*

A significant amount of work was done on the techno-economics of chemical looping combustion with oxygen uncoupling on biomass for the ETI's Techno-Economic Study of Biomass to Power with CO₂ capture (TESBiC) project. The report is based from the perspective of being able to deploy Biopower CCS by 2050. For this, 28 Biopower CCS technology combinations involving combustion or gasification of biomass (either dedicated or co-fired with coal) together with pre-, oxy- or post-combustion CO₂ capture were identified and assessed. In addition to the capital and operating costs, techno-economic characteristics such as electrical efficiencies (LHV% basis), Levelised Cost of Electricity (LCOE), costs of CO₂ captured and CO₂ avoided were modelled over time, assuming technology improvements from today to 2050. The report found that many of the Biopower CCS technologies gave relatively similar techno-economic results when analysed at the same scale, with the plant scale (MWe) observed to be the principal driver of CAPEX (£/MWe) and the co-firing % (i.e. the weighted feedstock cost) a key driver of LCOE. The data collected during the TESBiC project also highlighted the lack of financial incentives for generation of electricity with negative CO₂ emissions.

5.6 Chemical Looping Reformation

142. *IEAGHG 'Assessment of Emerging CO₂ Capture Technologies and their Potential to Reduce Costs', 2014/TR4, December 2014*

The IEAGHG 2014/TR4 report describes two types of natural gas reforming using chemical looping, based on steam reforming and autothermal reforming.

Steam Reforming Chemical Looping Combustion (SR-CLC) is essentially a steam methane reformer that uses Chemical Looping Combustion for reformer tube heating, so that the combustion flue gas is a mixture of CO₂ and water. For the purposes of this report, SR-CLC is considered to be equivalent to other forms of Chemical Looping Combustion, as described in Section 5.4.

Autothermal Chemical Looping Reforming (a-CLR), uses chemical looping technology to provide oxygen to an autothermal reformer (ATR) without the need for a cryogenic air separation unit. Thus, the technology development required for oxygen capture is the same as for Chemical Looping Combustion, but further integration is also required to deliver the oxygen into the ATR.

IEAGHG 2014/TR4 references a single laboratory test and assessed the technology readiness level as TRL-3. Wood has found other online references to isolated tests performed since 2014, but nothing that goes beyond the Ortiz paper referenced by TR4. Therefore, the technology readiness level is considered to remain at TRL-3.



6 Fuel Cell Carbon Capture

Use of fuel cells facilitates CO₂ capture either by performing a combustion-like reaction to generate electricity while keeping the fuel and oxidant streams separate, as in solid oxide fuel cell, or by moving CO₂ from the anode to the cathode, or by doing both, as in molten carbonate fuel cells.

The 2014 IEAGHG report has given technologies researched in this literature review a Technology Readiness Level (TRL). The following table summarises TRL's given to each technology by the IEAGHG in 2014 alongside the 2017 TRL estimated by Wood resulting from further developments in the literature.

Table 6-1: TRL for Fuel Cell CO₂ Capture Technologies

Technology	2014 TRL	2017 TRL
SOFCs	6	6
IGFC/IRFC and SOFC based power plant with CCS	4	5
MCFCs *	-	7
CCGT and MCFC based power plant with CCS *	-	5

* These technologies were not assessed in the IEAGHG 2014 report.

6.1 Solid Oxide Fuel Cells

143. IEAGHG 'Assessment of Emerging CO₂ Capture Technologies and their Potential to Reduce Costs', December 2014

This comprehensive review of novel CO₂ capture technologies includes a brief section on fuel cells which notes the inherent ability of some fuel cells to capture CO₂ while generating electricity. However, the report only covers a techno-economic assessment of Integrated Gasification Fuel Cell (IGFC) and Integrated Reforming Fuel Cell (IRFC) plant systems in which the carbon is removed upstream of a solid oxide fuel cell (SOFC) and does not cover the possibility of using MCFC's for post-combustion CO₂ capture.

The fuel cells themselves are given a technology readiness level of TRL-6 for large scale power generation due to being available at 60 kWe scale. However, the plant configuration including CO₂ capture is comparatively novel, although made up of components from IRCC and IGCC schemes and CO₂ purification units which may be similar to those required for oxy-combustion schemes. The NETL development work has continued since 2012, but appears to be mainly focussed on components of the scheme, particularly the SOFC.

Wood judge this to be a TRL level of 5 based on some components of the scheme being fully demonstrated, while others remain in pilot scale while the overall scheme remains theoretical.

6.2 Molten Carbonate Fuel Cells

The Molten Carbonate Fuel Cells themselves are already deployed in commercial service, including heat integration and use as combined heat and power units in the tens of MWe scale. Wood estimates that the readiness level of the MCFCs themselves is TRL-7. However, as for the SOFC's, above, a number of the components of the integrated NGCC with MCFCs for post-combustion capture are demonstrated at scale, or at sub-scale, but not the overall integrated scheme. Our estimate for the overall scheme therefore, is currently TRL-5, rising to 6 once the testing of flue gas CO₂ capture on FuelCell Energy's 2.8 MW stack is completed.

144. International Journal of Greenhouse Gas Control, "CO₂ Capture from Combined Cycles Integrated with Molten Carbonate Fuel Cells", by Stefano Campanari, Paolo Chiesa & Giampaolo Manzolini of Politecnico di Milano, December 2009



145. *International Journal of Hydrogen Energy*; “CO₂ Cryogenic Separation from Combined Cycles Integrated with Molten Carbonate Fuel Cells”, by Paolo Chiesa, Stefano Campanari & Giampaolo Manzolini of Politecnico di Milano, October 2010
146. *GHGT-10 “Application of MCFCs for Active CO₂ Capture within Natural Gas Combined Cycles”*, by S. Campanari, P. Chiesa & G. Manzolini of Politecnico di Milano, A. Giannotti, F. Federici, P. Bedont & F. Parodi of Ansaldo Fuel Cells S.p.A., 2011
147. *Applied Energy*, “Using MCFC for High Efficiency CO₂ Capture from Natural Gas Combined Cycles: Comparison of Internal and External Reforming”, by Stefano Campanari, Giampaolo Manzolini & Paolo Chiesa of Politecnico di Milano, February 2013
148. *Applied Energy*, “Economic Analysis of CO₂ Capture from Natural Gas Combined Cycles Using Molten Carbonate Fuel Cells”, S. Campanari, P. Chiesa, G. Manzolini of Politecnico di Milano & S. Bedogni of Edison SpA, April 2014

This series of papers from Politecnico di Milano and supporting companies cover a range of flow schemes for integrating Molten Carbonate Fuel Cells (MCFCs) into a natural gas turbine combined cycle power plant in a post-combustion CO₂ capture scheme. The MCFC is placed between the GT turbine exhaust and the heat recovery steam generator (HRSG) since it operates at 500-700°C, thus minimising any requirements for preheating and cooling. This provides a significant thermodynamic benefit over the application of MCFCs to coal based power production, where the exhaust gas must be cooled and cleaned before it can be fed to the MCFCs.

Main options covered include internal versus external reforming step and cryogenic versus oxyfuel removal of impurities from the CO₂ rich anode exhaust stream.

In all of these papers, the fuel cells themselves are relatively generic, with their performance predicted by theoretical analysis, modelling and backed up by some testing. The CO₂ captured or avoided varies from 57% to 85%.

149. *FUELCELL2015 (Proceedings of the ASME 2015 13th International Conference on Fuel Cell Science, Engineering and Technology)*, “Molten Carbonate Fuel Cells as Means for Post-Combustion CO₂ Capture: Retrofitting Coal-Fired Steam Plants and Natural Gas-Fired Combined Cycles”, by Maurizio Spinelli, Stefano Campanari, Matteo C. Romano & Stefano Consonni of Politecnico di Milano, Thomas G. Kreutz of Princeton Environmental Institute, Hossein Ghezal-Ayagh, Stephen Jolly & Matthew Di Nitto of Fuel Cell Energy, Inc., July 2015

This paper is also developed by the Politecnico di Milano team, but with input from Fuel Cell Energy, the manufacturers of the largest available fuel cells on the market (2.8 MW units) with substantial numbers of operating hours. Their largest site boasts a capacity of 59 MW.

The figures presented in this paper show high performance for the fuel cells themselves and some extremely useful installed capital and replacement cost information, but lower overall plant efficiency relative to the cases where the MCFC is integrated between the GT and HRSG. This paper also presents a coal flue gas case, with both cases resulting in 82% CO₂ capture.

150. *LEAP “CCP Novel CO₂ Capture technology Evaluation: WP1 MCFC package”*, by S. Consonni, F. Viganò, E. Martelli, M. Gatti, D. Di Bona, F. Capra, R. Scaccabarozzi, M. Gabba & M. Spinelli, April 15th, 2016
151. *CO₂ Capture Project “Evaluation of Five Alternative CO₂ Capture Technologies with Insights to Inform Further Development” presented at GHGT-13, Lausanne, Switzerland*, by Jonathan Forsyth, Stuart Lodge, Stefano Consonni, Daniele Di Bona, Manuele Gatti, Emanuele Martelli, Roberto Scaccabarozzi, Federico Vignano, November 2016

The Carbon Capture Project (CCP) have evaluated a number of schemes using MCFCs for CO₂ capture from natural gas fired combined cycle plants. These references detail their results comparing cases with and without exhaust gas recirculation and varying the destination of the unconverted hydrogen and CO recovered in the cryogenic purification system.

Since the cases where the recovered gases were returned to the fuel cell, rather than the GT, resulted in higher efficiency, the fuel cell was selected as the destination for the fuel gas recycle,



making the designs presented in this study slightly different from those presented in the earlier Politecnico di Milano reports.

152. *Publicity material from Fuel Cell Energy at <http://www.fuelcellenergy.com/assets/DFC-Carbon-Capture-White-Paper.pdf>*

The White Paper available on Fuel Cell Energy's website gives some useful key performance figures for their fuel cells when applied to CO₂ capture service, such as the mass flow rate of CO₂ moved from cathode to anode for a given size of cell, although large scale tests with CO₂ capture are only just due to start on one of their 2.8 MW units. There is a graph of the capacity of fuel cells required for a given CO₂ capture level for different type of plants.



7 Summary of Technology Readiness Levels

For this study, Wood has reviewed the carbon dioxide capture technologies identified in the IEAGHG 2014/TR4 report 'Assessment of Emerging CO₂ Capture Technologies and Their Potential to Reduce Costs' and has investigated more recent publications that may describe advances in the intervening three years. Table 7-1 below indicates the Technology Readiness Level (TRL) assigned by IEAGHG to each technology in 2014 and the corresponding assessment of Wood in 2017. This indicates that some progress has been made in developing some low-TRL processes and demonstrating them at laboratory or pilot-plant level. Much of this has resulted from the wide-ranging programme of coal-based power research in the USA, funded by the Department of Energy. Many potential processes exist. Developing these to the point of commercialisation presents a significant challenge in a world that takes fossil-fuel power generation for granted.

Table 7-1: TRL for All Carbon Dioxide Capture Technologies Assessed

Technology	2014 TRL	2017 TRL
Post-Combustion Processes		
Conventional Solvents	9	9
Improved Conventional Solvents	6-8	6-8
Encapsulated Solvents	1	2-3
Precipitating Solvents	4-5	4-5
Biphasic Solvents	4	4
Ionic Liquids	1	1
Algae Based Capture	1	3
Polymeric Membranes	6	6
Polymeric Membranes / Cryogenic Separation Hybrid	6	6
Room Temperature Ionic Liquid (RTIL) Membranes	2	2
Vacuum Pressure Swing Adsorption (VPSA)	3	3
Temperature Swing Adsorption (TSA)	1	7
Molecularly Imprinted Polymer Particle CO ₂ Sorbents *	-	1-2
Enzyme Catalysed Adsorption	1	6
Amine Catalysed Adsorption *	-	6
Electrochemically Mediated Adsorption	1	1
Mineral Carbonation *	-	5
Cryogenic Capture	3	4
Supersonic Inertia Capture	1	3
Pre-Combustion Processes		
Conventional Solvents for Natural Gas Treating	9	9
Conventional Solvents for Hydrogen Purification *	-	9
Gas Separation Membranes for Natural Gas Treating *	-	8
Gas Separation Membranes	5	5
Physical Separation	2	7



Technology	2014 TRL	2017 TRL
Pressure Swing Adsorption *	-	9
Vacuum Swing Adsorption *	-	8
Low Temperature Separation of CO ₂ from Natural Gas *	-	7
Low Temperature Separation of syngas	2	2
Oxy-combustion Processes		
Oxy-fired Circulating Fluid Bed Boiler (coal)	7	7
Oxy-fired Pulverised Coal Boiler	7	7
Oxy-combustion Flue Gas Purification Units	5-6	5-6
Oxy-fired Gas Turbine Cycles (Allam Cycle)	2	7
Oxy-fired Gas Turbine Cycles (CES Cycle)	5	5
Oxy-fired Gas Turbine Cycles (Others)	2	2
Chemical Looping Processes		
Post-Combustion Calcium Looping	6	6-7
Sorbent-Enhanced Water Gas Shift (SEWGS)	5	5
Chemical Looping Combustion	2	6-7
Chemical Looping Combustion with Oxygen Uncoupling	1	2-3
Chemical Looping Steam Reforming	3	3
Fuel Cell Processes		
Solid Oxide Fuel Cells (SOFC)	6	6
IGFC/IRFC and SOFC based power plant with CCS	4	5
Molten Carbonate Fuel Cells (MCFC) *	-	7
CCGT and MCFC based power plant with CCS *	-	5

* These technologies were not assessed in the IEAGHG 2014/TR4 report.

