



Programme Area: Carbon Capture and Storage

Project: Hydrogen Turbines Follow On

Title: A Review of Selected New CO₂ Capture Technologies

Abstract:

Development aspects and assessments of Gas Turbines (fired by methane and/or H₂) are provided, including contemporary OCGT GTs from GE. Additionally, potentially synergistic capture technologies are described.

Context:

Carbon capture from GTs is relatively expensive, mostly because the lean burn technologies produce a flue gas very dilute in CO₂, needing a voracious solvent and very large equipment. This package is a collection of background papers for exploring ways in which the capture technology could be assisted by GT choice, or configuration. One way of concentrating the CO₂ is in precombustion technologies, so use of H₂ in GT is also included.

A REVIEW OF SELECTED NEW CO₂ CAPTURE TECHNOLOGIES

**Report for
Energy Technologies Institute**

November 2016

**John Davison
Energy Consultant
Cheltenham, UK**

Disclaimer

The information in this report is provided "as-is," and all warranties, express or implied, are disclaimed (including but not limited to the disclaimer of any implied warranties of merchantability and fitness for a particular purpose). The information may contain inaccuracies, errors, problems or other limitations. The reader agrees that the author is not liable for any damages whether actual, direct, indirect, special, incidental, consequential damages or any other damages (including damages for loss of business, loss of profits, litigation, or the like), or whether based on breach of contract, breach of warranty, tort (including negligence), product liability or otherwise, arising in any way from use of the information in this report even if advised of the possibility of such damages. No representations, warranties or guarantees whatsoever are made as to the accuracy, adequacy, reliability, currentness, completeness, suitability or applicability of the information to a particular situation. References herein to any commercial product, process, service or trade name, trade mark or manufacturer does not necessarily constitute or imply any endorsement, recommendation or any favouring of such products.

INDEX

Executive Summary	1
1. Introduction	3
1.1 Background	3
1.2 Scope of the assessment	3
1.3 Metrics for assessment of capture technologies	3
2. Membranes for post combustion capture	5
2.1 Process description	5
2.2 Energy requirement and costs	7
2.3 Development status and TRL	8
3. Molten carbonate fuel cells with CO₂ capture	8
3.1 Process description	8
3.2 Energy requirement and costs	10
3.3 Development status and TRL	12
4. Cryogenic separation	12
4.1 Refrigerated capture processes	13
4.1.1 Process description	13
4.1.2 Energy requirement and costs	14
4.1.3 Development status and TRL	15
4.2 Supersonic inertial separation	16
4.2.1 Process description	16
4.2.2 Energy requirement and costs	17
4.2.3 Development status and TRL	17
5. Bi-phasic solvent scrubbing	17
5.1 Bi-phasic liquid-liquid processes	18
5.1.1 Process description	18
5.1.2 Energy requirement and costs	18
5.1.3 Development status and TRL	19
5.2 Bi-phasic liquid-solid scrubbing	19
5.2.1 Process description	19
5.2.2 Energy requirement and costs	20
5.2.3 Development status and TRL	21
6. Potassium carbonate scrubbing	21
6.1 Scrubbing at elevated pressure	21
6.1.1 Process description	21
6.1.2 Energy requirement and costs	22
6.1.3 Development status and TRL	22
6.2 Potassium carbonate scrubbing with precipitation	23
6.2.1 Process description	23
6.2.2 Energy requirement and costs	23
6.2.3 Development status and TRL	24
7. References	25

EXECUTIVE SUMMARY

A review has been undertaken of selected CO₂ capture processes that are of interest to the ETI. The review provides descriptions of the technologies and outline discussion of the energy consumption, costs, percentage capture and development status, based on information in the public domain. The processes selected by the ETI were:

1. Post combustion capture membranes
2. Molten carbonate fuel cells for post combustion capture
3. Cryogenic separation (refrigerated and supersonic inertial separation)
4. Bi-phasic solvent scrubbing (liquid-liquid and liquid-solid)
5. Potassium carbonate scrubbing (pressurised and precipitating)

The performance, costs and status of the capture processes in coal fired power plants are summarised in Table 1. In most cases the process developers have quoted relative improvements compared a baseline of MEA solvent scrubbing and this is the way the information is presented in Table 1. It should however be noted that CCS demonstration power plants are being built and operated using commercial solvents which have lower energy consumptions than MEA, resulting in power plant thermal efficiencies around 3 percentage points higher.

Most of the processes offer the prospect of efficiency improvements compared to MEA scrubbing in the range of 1-4 percentage points but molten carbonate fuel cells and refrigerated cryogenic separation are predicted to have greater improvements, in the range of 5-7 percentage points. Most of the processes considered in this report are claimed to give around 10 percent lower costs of electricity but molten carbonate fuel cells and cryogenic separation are claimed to reduce the electricity cost by of the order of 25%. It should be emphasised that the performance and cost data are subject to significant uncertainty because the technologies are still at an early stage of development. In general, costs of new technologies tend to increase as they progress from early stage development to commercial application and some of the processes are likely to fail to achieve their expected or targeted performance and costs. Indeed, the expected performance and costs of some of the processes have already been seen to become less favourable during development.

Most of the processes are aimed at the current norm of 90% capture, although supersonic separation has so far not met this target. The percentage capture is not necessarily fixed and could in most cases be increased at higher cost. The refrigerated cryogenic process appears to be particularly suitable for higher percentage capture.

The processes are mostly at the laboratory to small pilot plant scale of development (TRL 3-6). A larger scale pilot plant or plants would be required before a full size commercial plant could be built.

The development programmes have focussed mainly on coal fired power plants, which have so far been the main target for CCS. There is now increasing interest in general in application of CCS to gas fired power plants and various other industrial plants. The new capture technologies could in principle be applied to many of these other types of plants which are characterised by different flue gas CO₂ concentrations and impurities but the relative merits of the technologies may be different. Further evaluation is needed to quantify the differences.

Table 1 Summary of process performance, costs, development status and challenges

	CO ₂ Capture	Power Plant Efficiency	Cost of Electricity	TRL	Main development challenges
	%	% point increase vs MEA baseline	% reduction vs MEA baseline		
Membranes	90	3-4	9-13	6	Membrane throughput, selectivity, durability, scale-up and costs
Molten carbonate fuel cells with capture	92	7	25	4	Reduction of fuel cell CAPEX and fuel cell scale-up, impacts of impurities and durability
Cryogenic (refrigerated)	90-99	5-7	16-33	5	Handling solid CO ₂ and avoiding blockages, heat integration to minimise energy usage
Cryogenic (supersonic)	90 (target)	1-2	10	3	Formation of particles sizes to achieve target percentage capture, minimising gas compression, handling solid CO ₂
Bi-phasic liquid-liquid	90	1-4	7	4	Confirm solvent performance, solvent decanting
Bi-phasic liquid-solid	90	3	13	4	Solvent performance, solids handling
Potassium carbonate	90	3	13	5	Solvent additive performance, solids handling

Performance and cost data for pulverised coal fired power plants.

1. INTRODUCTION

1.1 Background

Work undertaken by the Energy Technologies Institute (ETI) and others has shown that successful deployment of carbon capture and storage (CCS) would substantially reduce the costs of providing low carbon electricity and reducing emissions from industry and other sectors of the economy. Costs of CCS can be reduced without creating new capture technology platforms, by making use of economies of scale, sharing infrastructure and risk reduction through deployment. After 2030, technology innovation should play an increasing role in ongoing cost reduction (ETI, 2016).

1.2 Scope of the assessment

Research and development is being undertaken on a wide range of new CO₂ capture technologies. This report provides a review of the following post combustion capture technologies selected by the ETI, their potential for reduction of energy consumption and costs and their development status.

1. Post combustion capture membranes
2. Molten carbonate fuel cells for post combustion capture
3. Cryogenic separation (refrigerated and supersonic inertial separation)
4. Bi-phasic solvent scrubbing (liquid-liquid and liquid-solid)
5. Potassium carbonate scrubbing (pressurised and precipitating)

The report assesses the technologies mainly in the context of coal fired power generation plants, as that is the basis of most publications and development programmes for the technologies. The importance in future of gas fired power generation and industrial applications of CCS are however being increasingly recognised. The technologies evaluated in this report would in principle also be suitable for many such applications and comments about their suitability are included in the report.

The assessments of technologies in this report are based on non-proprietary information mainly from publications that are in the public domain. If ETI is to make any decisions with commercial implications it is recommended that they should seek further information from the process developers under a confidentiality agreement to confirm or refute any conclusions drawn from this report.

1.3 Metrics for assessment of capture technologies

Thermal efficiency and base load levelised cost of electricity (LCOE) are normally the main metrics used to assess new CO₂ capture technologies for power plants. These criteria are normally assessed in comparison to a baseline capture technology. Most publications assume the baseline is mono-ethanolamine (MEA) scrubbing, because this is a well understood process for which extensive information is available in the public domain. It should however be noted that the leading post combustion capture demonstration plants such as Boundary Dam and Petra Nova use proprietary solvents which have significantly lower energy consumptions than MEA. For example, in NETL's Revision 2 Baseline Study (NETL, 2010) the efficiency of a supercritical coal fired power plant with MEA scrubbing is 10.9 percentage points (HHV basis) lower than that of a comparable plant without capture but in NETL's most recent Revision 3 study (NETL, 2015), which is based on Cansolv solvent

scrubbing, the efficiency difference between supercritical coal fired plants with and without capture is 8.2 percentage points.

The costs of baseline amine scrubbing technologies are likely to decrease in future as they progress along the well-established cost reduction curve, due to learning-by-doing and incremental improvements. Although some of the learning will be transferable to new capture technologies, some of it may not. New capture technologies could therefore be regarded as chasing a moving target of baseline technologies. The new technologies will therefore need to show significant improvements over the established capture technologies to make their development commercially viable and to overcome the perceived higher short term risks of new technologies.

In this report each of the capture technologies is assigned a Technology Readiness Level (TRL). The definitions of TRL levels proposed by EPRI (Freeman, 2011) shown in Table 2 have been used.

Table 2 Technology Readiness Level (TRL)

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

It should be recognised that there are alternative definitions of TRL levels and assigning a TRL to a technology is subjective. As well as the criteria set out in Table 1, some organisations also stipulate a minimum scale of operation for each TRL stage but for the purposes of this report no quantified minimum scales have been applied.

One of the criticisms of the TRL framework is that it does not show the amount of effort and time required to achieve later TRL levels and the probability of success. This may depend on for example whether the process uses equipment and techniques that are already used in other well established process or whether new materials and fundamentally new equipment needs to be developed to progress to later TRLs.

This report focuses on efficiency and base load LCOE which have traditionally been the main metrics for evaluating capture technologies. It is however being increasingly recognised that in future low carbon electricity systems, power plants with CCS will have to operate flexibly and at lower annual capacity factors to enable the system to cope with variability in electricity demand and output from renewable generation technologies. Indeed, the ability to operate flexibility is expected to be one of the features that will make CCS an attractive technology. Operating flexibility depends on aspects of detailed design which are not normally available at early stages of technology development, so it is not possible to make definitive statements about flexibility in this review. The relative importance of

capital and operating costs is different for base load and lower capacity factor power plants and this can affect the relative merits of different capture technologies. For plants that will operate at low capacity factors, thermal efficiency becomes relatively less important and capital cost becomes more important.

An important issue for industrial applications is the form in which energy is supplied to drive the CO₂ capture process. In amine scrubbing technologies most of the energy is provided in the form of low pressure steam, which can be extracted relatively easily from the steam turbine of a power plant. Some industrial processes have surplus low grade heat which may be suitable for providing the energy for CO₂ capture. However most industrial processes do not have access to sufficient surplus heat, so boilers or combined heat and power plants would need to be built, which can be inconvenient and relatively expensive and inefficient compared to utility scale power plants. In such cases, processes which use electricity to provide the energy for separation would tend to be preferred. Some new capture technologies use relatively small modules, which would make them more attractive in smaller scale industrial applications, compared to technologies that can be easily scaled up to large single modules.

2. MEMBRANES FOR POST COMBUSTION CAPTURE

2.1 Process description

A membrane is a semi-permeable barrier that selectively permits passage of components of a mixture. Transport of a component through a membrane requires a driving force, typically a partial pressure or concentration difference. The selectivity depends on the relative rates at which chemical species permeate.

Polymeric membranes have been used for industrial scale gas separation for many years, for example for CO₂ separation from natural gas and hydrogen recovery from ammonia. Polymeric membranes have the advantages of not producing hazardous wastes, they are modular which allows for scale-up, and their energy requirement is in the form of electricity for gas compression, which may be more convenient than low pressure steam at some industrial sites and retrofits.

The driving force for CO₂ flow through polymeric post combustion CO₂ capture membranes is the partial pressure on either side of the membrane. If the aim is to separate a high concentration stream of CO₂, the total pressure of the separated CO₂ needs to be lower than the partial pressure in the flue gas. The separated CO₂ then needs to be compressed, which accounts for much of the energy consumption of the membrane separation process. To avoid having to operate the final stages of membrane at very low pressure, an alternative approach shown in Figure 1 can be used. In this configuration a first stage membrane is used to separate part of the CO₂, followed by a second stage "air sweep" membrane which makes use of the low partial pressure of CO₂ in air to provide the driving force for separation, rather than vacuum. The CO₂-enriched air from this membrane is used as combustion air in a boiler or gas turbine. The CO₂ recycled in the combustion air increases the CO₂ concentration in the boiler flue gas, which provides an additional advantage of a greater driving force for separation in the first stage membrane, and hence an even lower CO₂ compression power consumption. Use of air sweep has the potential to lower the CO₂ capture energy penalty significantly, by 5% of the total plant output or more (Merkel, 2010). A disadvantage is that the boiler air fan power consumption increases and there is a small decrease in the energy efficiency of the boiler.

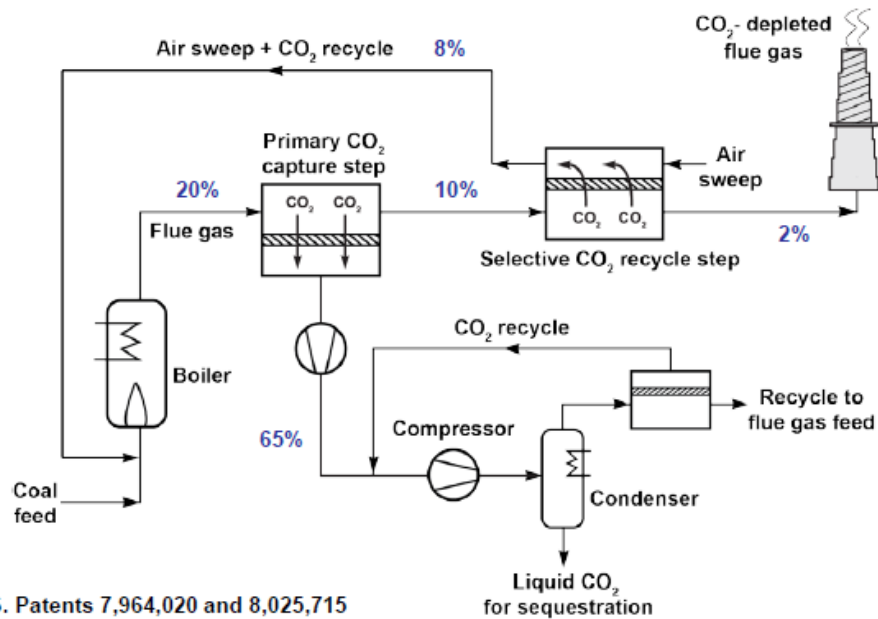


Figure 1 MTR membrane system with air sweep (Knief, 2016)

(Note: the percentages are the CO₂ concentrations)

A limitation of CO₂ capture membranes is that, depending on the selectivity, the concentration of the separated CO₂ can be less than that required for pipeline transmission and storage, so a purification process is needed, typically a further high pressure membrane stage as shown in Figure 1, or low temperature separation.

Membranes can also be used in combination with amine scrubbing. A configuration involving membranes followed by amine scrubbing as a final stage to achieve a high percentage capture rate has been proposed (Kundu, 2014). An alternative that is being developed by Membrane Technology & Research (MTR) and the University of Texas is to use solvent scrubbing as the first stage, followed by an air sweep membrane as a second stage, with the outlet gas recycled to the boiler (hybrid-series arrangement) or a configuration that involves feeding part of the flue gas to a solvent scrubber and the rest to an air-sweep membrane (hybrid parallel arrangement) (Freeman, 2014a; 2016). Both of these arrangements provide flue gas with a higher CO₂ concentration to the solvent scrubbers. A hybrid-parallel arrangement for selective exhaust recirculation (EGR) as shown in Figure 2 could enable the CO₂ concentration in flue gas from a gas turbine combined cycle plant to be increased to 15-20%, thereby substantially reducing the quantity of flue gas going to the capture unit and potentially reducing its energy consumption (Freeman, 2014b).

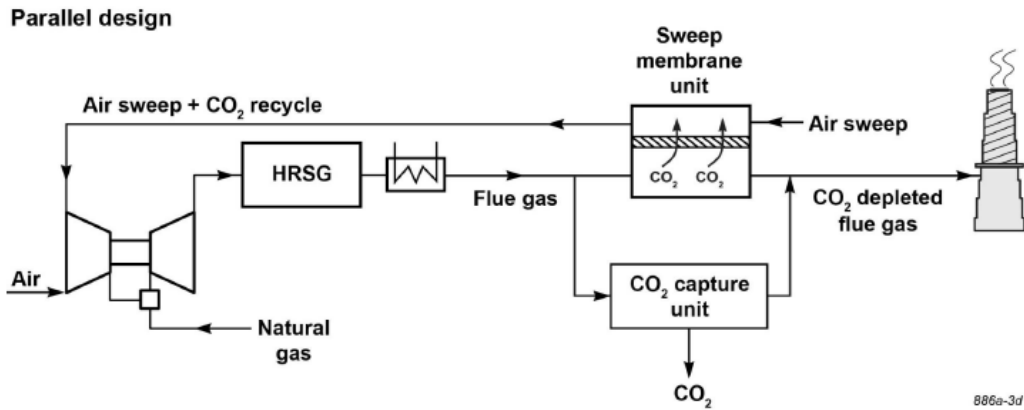


Figure 2 Sweep-assisted hybrid-parallel design for selective EGR (Freeman, 2014b)

Another configuration that is being researched, for example by Air Liquide with DOE funding, involves operating the membranes at low temperature (-35C to -45C), which increases the membrane CO₂/N₂ selectivity and permeance. However this concept is more complicated, it requires a particular type of membrane material and requires significant heat and work integration. Flue gas is compressed to 16bar prior to cooling and separation and the flue gas is expanded to recover energy after CO₂ separation (Augustine, 2016).

Another type of membrane is the supported liquid membrane (SLM), which consist of a liquid phase containing a carrier species in the pores of a polymer support. Liquid membranes can achieve >90% CO₂ capture and high CO₂ purity in a single stage. However, these systems are relatively unstable as the carriers can be washed out from the system as they are not bonded to the polymer matrix. Ionic liquids are favourable as they have high temperature durability and negligible volatility. Another type of membrane is the fixed carrier membrane, where the reactive group is bound to the polymer backbone of the membrane material. Fixed site carrier membranes combine the durability of solid polymeric membranes with the selectivity of SLM, and at the same time overcome the limitation of SLM, i.e. the degradation due to the wash-out of the carrier solution over time.

Coal fired power plants present some challenges for membranes. Particulate matter can deposit on the membrane surface decreasing its permeability or damaging it over time. Another issue is that membranes are a modular technology and utility scale power plants will require the flue gas to be distributed across a large number of membrane modules. Good sealing of membranes is needed to avoid leakage of flue gas into the CO₂, which reduces the CO₂ purity.

2.2 Energy requirement and costs

A study by NETL estimated that use of MTR membranes at a supercritical coal fired power plant would reduce the energy efficiency penalty for CO₂ capture by 4.3 percentage points compared to MEA scrubbing and reduce the cost of electricity by 12.6% (NETL, 2012). This study is based on the configuration shown in Figure 1. The costs were estimated based on a future membrane cost of 80\$/m³ and replacement time of 5 years, compared to near term performance objectives of 150\$/m³ and 4 years. An updated techno-economic assessment is underway

Air Liquide's cold membrane system is reported to have an energy consumption of 320-332 kWh/t CO₂ and a cost of 42-48\$/t CO₂, compared to 56\$/t for NETL's supercritical coal plant with MEA scrubbing (Chaubey, 2016). This is equivalent to a 3 percentage point reduction in efficiency penalty for capture and a 9% reduction in LCOE compare to NETL's baseline MEA plant.

The energy consumptions and costs of polymeric membranes are significantly higher for natural gas combined (NGCC) plants due to the lower CO₂ concentration in the flue gas. An efficiency of 35% is predicted for a plant with 90% CO₂ capture, increasing to 45% if the gas turbine includes exhaust gas recycle (EGR). This is substantially lower than a plant with MEA scrubbing (Jordal, 2016). Partial capture is suggested as a potentially attractive option for membranes at NGCCs. The efficiency penalty for 60% capture is reported to be around 4 percentage points without EGR.

The use of air-sweep membranes and selective exhaust gas recirculation to provide 88% CO₂ avoidance in a gas turbine combined cycle plant was assessed (Forsyth, 2016). The thermal efficiency was predicted to be 48%, i.e. 10 percentage points lower than a plant without capture and 2 percentage points lower than a plant with MEA scrubbing. The cost of CO₂ avoidance using membranes was estimated to be 15% higher than using MEA scrubbing.

MTR has shown that reducing the percentage capture rate would reduce the specific energy consumption of a hybrid membrane capture process. Reducing the capture rate from 90% to 50% reduces the thermodynamic minimum energy of separation per mole of CO₂ captured from coal fired power plant flue gas (13% CO₂ concentration) by 18% (Freeman, 2014b).

2.3 Development status and TRL

MTR has undertaken over 1,000 hours of tests in a 1MW_e (20t/d CO₂) pilot unit at the National Carbon Capture Centre) in Alabama using flue gas from a coal fired boiler. This qualifies the technology as TRL 6. Over 11,000 hours of smaller scale testing using coal-derived flue gas has also taken place. The 20t/d pilot plant is being installed at B&W's boiler research facility. This will represent the first integrated boiler/membrane operation where CO₂ enriched air is selectively recycled to an appropriately-sized boiler (Kniep, 2016).

Bench scale testing of a hybrid process consisting of membrane separation and solvent scrubbing is being carried out in collaboration with the University of Texas (Freeman, 2016).

Polymeric polyvinylamine fixed site membranes were tested using flue gas from a coal fired power plant at Sines, Portugal as part of the EU Nanoglowa project (Sandru, 2013).

Air Liquide's cold membrane process has been operated at a 0.1MW_e scale using synthetic flue gas (TRL 4). An on-going project is testing the technology at a 0.3MW_e scale using real flue gas at the National Carbon Capture Centre in Alabama, which will result in a TRL 5 classification if successful (Chaubey, 2016).

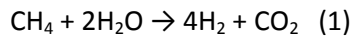
Challenges for post combustion capture membranes include obtaining good membrane selectivity and permeance and acceptable fouling and/or plugging, sealing, membrane costs and equipment lifetimes.

3. MOLTEN CARBONATE FUEL CELLS WITH CO₂ CAPTURE

3.1 Process description

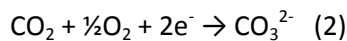
Molten carbonate fuel cells are being developed and commercialised for power generation and they are also being developed to enable them to additionally capture CO₂ from external sources of flue gas, as shown in Figure 3.

In commercially available molten carbonate fuel cells (MCFC) a fuel, usually natural gas, is supplied to an internal catalytic reformer on the anode side of the fuel cell, where it is reformed by reacting with steam to produce CO_2 and H_2 according to equation 1.

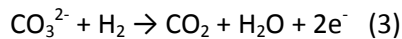


Reforming can be carried out externally but including it within the fuel cell is advantageous because the heat released by the fuel cell's other reactions can provide the endothermic heat required by the reforming reactions.

CO_2 and O_2 are supplied to the cathode, where they react to produce carbonate ion according to equation 2:



The carbonate ion passes through a carbonate electrolyte to the anode where it reacts with H_2 , producing CO_2 , H_2O and free electrons according to equation 3.



As well as CO_2 and H_2O , the off-gas from the anode also contains unreacted fuel (CH_4 , CO and H_2). The unreacted fuel can be separated from this stream and recycled to the fuel cell or be thermally oxidised to produce heat.

In a conventional MCFC, the CO_2 for reaction 2 is derived from the anode off-gas and the O_2 is supplied by air but an alternative, as shown in Figure 3, is to use flue gas from a separate combustion plant such as a gas turbine or coal-fired boiler to provide both the CO_2 and some or all of the O_2 . In this way the fuel cell produces a concentrated stream containing not only the CO_2 produced from its own fuel but also most of the CO_2 contained in the externally supplied flue gas. NGCC flue gas contains sufficient O_2 but for flue gas from a coal fired boiler some air would also need to be fed to the cathode. The driving force for CO_2 separation is electrochemical potential rather than pressure differential across the membrane.

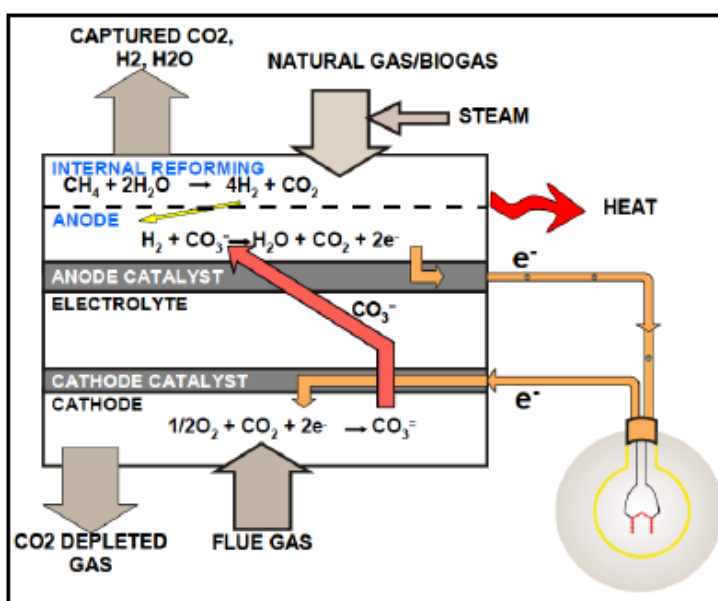


Figure 3 Electrochemical Membrane fuel cell (Ghezel-Ayagh, 2016)

A molten carbonate fuel cell with CO₂ capture is being developed by Fuel Cell Energy, based on their commercial Direct FuelCell® system. The fuel cell with CO₂ capture is known as an Electrochemical Membrane (ECM) and the overall system is known as CEPACS (Combined Electric Power and Carbon Dioxide Separation). In an overall system flowsheet presented by Jacobs (Jacobs Consultancy, 2015) the flue gas feed to the ECM is cooled to condense water before being preheated firstly by heat exchange with the anode and cathode off-gases and then by catalytic oxidation of some of the unconverted fuel and hydrogen. The ECM operating temperature is 550-650C. The CO₂-rich anode off-gas is partially cooled and passed through a low temperature shift converter where most of the CO is reacted with steam to produce hydrogen and CO₂. It is then cooled, compressed and the CO₂ is liquefied. Some of the unreacted fuel components separated from the CO₂ are used to heat the cathode feed gas and the rest is mixed with the fuel input stream fed to the anode. Due to the planar geometry and large gas flow channels, ECM can process large gas volumes without significant back pressures.

Impurities in flue gas can significantly damage MFCs (Wee, 2014). It is proposed that for flue gas from coal fired plants a polishing FGD unit should be installed upstream of an ECM, resulting in for example a SO_x concentration of <1ppmv. Bench scale tests of over 600 hours each have been carried out to investigate any impacts of impurities on the fuel cell. The tests were conducted with 1 ppm SO_x in the flue gas feed and levels of mercury, selenium and HCl substantially higher than would be expected in coal plant flue gas. Short term exposure to substantially higher than normal levels of SO₂, (40ppm) and also Se, Hg and HCl were assessed in bench scale tests and there was reported to be no apparent irreversible degradation.

The fuel cell materials are not expected to be degraded by NO_x and tests have shown >70% destruction of NO_x at high concentrations in the inlet flue gas (200ppm) (Ghezel-Ayagh, 2016). NO and NO₂ are converted to NO₂⁻ and NO₃⁻ at the cathode and they are transferred to the anode where they are converted to N₂. The percentage NO_x destruction is higher at lower inlet NO_x concentrations.

3.2 Energy requirement and costs

As part of a DOE contract AECOM estimated the efficiency and costs of Fuel Cell Energy ECM plants. The costs were compared to NETL's Revision 2 baseline supercritical coal fired power plants with and without MEA capture (NETL, 2010). An ECM plant capturing 90% of the CO₂ from the flue gas of a 550MW pulverised coal power plant would generate an additional 319 MW of net electricity and the overall plant would have an efficiency of 40.7% (Ghezel-Ayagh, 2016). The marginal efficiency of the ECM unit would be 43.4% (HHV basis).

Analysing the energy consumption and costs of using fuel cells for CO₂ capture is less straight forward than for most capture technologies because as well as capturing CO₂, the fuel cells also generate substantial amounts of extra power and they use a fuel that may be different to that used to produce the external source of flue gas. In order to compare the efficiencies of the ECM technology and post combustion solvent scrubbing it is necessary to calculate to what extent the efficiencies of coal and gas fired power plants with solvent scrubbing would need to improve in order generate the same total power output as a PC+ECM plant, assuming the same amounts of coal and natural gas fuel inputs in both cases. In order to match the overall power output of a PC+ECM power plant as described above (Ghezel-Ayagh, 2016) , the efficiencies of coal and gas fired power

plants with solvent scrubbing would both need to be 7.3 percentage points higher than NETL Rev.2 plants based on MEA scrubbing.

The efficiency advantage of the ECM technology depends on the efficiency of the baseline natural gas combined cycle power plant. Future increases in the efficiencies of gas turbine combined cycles would reduce the efficiency advantage of the ECM technology. For example, an increase of 5 percentage points in the efficiency of combined cycle plants would reduce the efficiency advantage of the ECM technology applied to coal power plant flue gas from 7.3 to 5.6 percentage points compared to MEA scrubbing, but this is however still substantial.

The LCOE of an ECM equipped power plant is reported to be 31% lower than a coal-fired plant with MEA scrubbing (Ghezel-Ayagh, 2016). The ECM equipped plant should however be compared to a combination of coal and gas fired plants with amine scrubbing, because the ECM equipped plant uses both coal and gas fuels. On this basis the LCOE of ECM equipped plants would be around 25% lower than the weighted average of coal and gas fired plants using MEA scrubbing.

The relative costs of solvent scrubbing and fuel cell plants depend strongly on the capital costs and lifetimes of fuel cells. A publication by Politecnico di Milano and Edison SpA (Campanari, 2014) showed high thermal efficiencies for MCFCs with CO₂ capture but costs were reported to be not currently competitive with MEA scrubbing. The work showed that 75-80% of CO₂ can be captured from a natural gas combined cycle plant (NGCC) with small or negligible efficiency penalties (<0.2 percentage points) compared to a baseline NGCC without capture. Despite the favourable energy consumption, the cost of CO₂ avoidance for a NGCC+MCFC plant was more than twice that of a plant with MEA scrubbing, assuming a current MCFC total equipment cost of 2700 €/kW. CO₂ capture using MCFCs would be competitive if the MCFC cost fell in the range of 1000-1500 €/kW, depending on the price of natural gas.

ECMs would be well suited to various smaller scale CO₂ emission sources, because of the modular nature of fuel cells. Sites where there is no low pressure steam available for amine regeneration and where there is a demand for power would be particularly suitable. Jacobs Engineering carried out a study for Alberta Innovates which assessed MCFC capture of CO₂ at once-through steam generators that are widely used in Steam Assisted Gravity Drainage (SAGD) tar sands extraction operations (Hill, 2015). Fuel cell technical details and costs for this study were provided by Fuel Cell Energy. The capital cost of adding MCFC CO₂ capture was reported to be 73% of the cost of adding amine post combustion capture. The cost of CO₂ avoided, taking account of the prices and associated CO₂ emissions of imported and exported power, was 267 CAN\$ for amine scrubbing and 29 CAN\$ for the MCFC scheme. The MCFCs capture 93% of the overall CO₂. Because of the avoided emissions associated with the exported power, the overall net emissions of the scheme were reported to be negative.

An NGCC plant integrated with MCFCs with CO₂ capture is predicted to have an efficiency that is only 1 percentage point lower than an NGCC without capture, and 7 percentage points higher than an NGCC with an MEA capture process. The cost of CO₂ avoided is predicted to be 27% lower than for MEA scrubbing (Forsyth, 2016). It is however pointed out that the cost is dependent on new technology where there is low certainty on the figures. THE MCFC cost used in the estimation is much lower than current costs and is based on future mass-production of the stack components and packaging. The operating costs assume that the electrodes and electrolyte are resistant to degradation and capable of long service life.

Use of fuel cells for CO₂ capture in cement plant is another promising option which has been assessed (Spinelli, 2014).

3.3 Development status and TRL

Fuel Cell Energy's commercial Direct Fuel Cells without CO₂ capture have been operating since 2003 and it was reported in mid-2015 that over 100 plants were in operation (Ghezel-Ayagh, 2015). The largest power plant is a 59MW plant in Korea consisting of twenty one 2.8MW DFC3000 units. Substantially larger units would ideally be required for integration with utility scale power plants.

Feeding of flue gas to a fuel cell has only been tested at bench scale using simulated flue gas. The technology can therefore only be considered to be at TRL 4. By August 2016 Fuel Cell Energy's bench scale unit at Pacific North West Laboratory had operated for a run time of 15,700 hours (Ghezel-Ayagh, 2016). Various other organisations have also undertaken bench scale testing of CO₂ capture in MCFCs over a number of years (Wee, 2014; Rexed, 2015).

US DOE/NETL awarded funding for a project that will design, fabricate, and test a pilot-scale system, prototypical of a commercial unit, that incorporates a 2MW_e modified version of Fuel Cell Energy's DFC3000 fuel cell which will be used to capture CO₂ from a slipstream of flue gas from an existing coal fired power plant. The aim is to capture 90% of the CO₂ and achieve 95% CO₂ purity. The project will run from October 2015 to March 2019. Successful pilot scale validation of the system is expected to pave the path toward commercial deployment of cost-effective technology for large scale coal-based CO₂ capture applications by 2025 (DOE, 2015).

Early in 2016 Fuel Cell Energy announced a contract with Cenovus Energy to complete preliminary designs and engineering for siting a molten carbonate fuel cell system to capture 75% of the CO₂ from the flue gas from an existing 14 MW natural gas-fired turbine cogeneration facility at the University of Calgary, Alberta. The project aims to quantify the benefits of separating CO₂ from the flue gas of boilers used to make steam for oil sands production (Fuel Cells Bulletin, 2016).

In May 2016 Exxon and Fuel Cell Energy announced an agreement "to pursue novel technology in power plant carbon dioxide capture through a new application of carbonate fuel cells, which could substantially reduce costs and lead to a more economical pathway toward large-scale application globally". The scope of the agreement "will initially focus for about one to two years on how to further increase efficiency in separating and concentrating carbon dioxide from the exhaust of natural gas-fuelled power turbines. Depending on reaching several milestones, the second phase will more comprehensively test the technology for another one to two years in a small-scale pilot project prior to integration at a larger-scale pilot facility" (ExxonMobil, 2016).

4. CRYOGENIC SEPARATION

Cryogenic (low temperature) processes can be used for pre-combustion and post-combustion capture of CO₂. Pre and post combustion capture processes are substantially different. When flue gas at atmospheric pressure is cooled the CO₂ solidifies but at high pressures and concentrations, typical of pre-combustion capture, CO₂ can be separated as a liquid. Cryogenic separation of CO₂ using Air Liquide's CRYOCAP™ process was inaugurated in 2015 in an industrial scale reference plant (100kt/y CO₂) at a natural gas reforming hydrogen plant at Port Jérôme in France (Air Liquide, 2015). The CRYOCAP™ process is reported to reduce the cost of capture by 35% compared to aMDEA scrubbing (Terrien, 2014). ETI has experience of pre-combustion cryogenic capture of CO₂ as part of

a potential demonstration project. This review concentrates on post combustion cryogenic separation.

There are several variants of cryogenic post combustion capture, including refrigerated processes and supersonic inertial separation processes, which are described separately in this report. Cryogenic capture has the advantage of requiring no chemicals and it can also co-capture other pollutants such as SO_x, NO_x and mercury.

4.1 Refrigerated capture processes

4.1.1 Process description

The temperature to which flue gas needs to be cooled depends on the percentage capture of CO₂. For coal fired power plant flue gas, about 90% capture can be achieved at -120C and 99% at -132C (Baxter, 2014).

Ecole des Mines de Paris, in collaboration with Alstom, has researched temperature swing cryogenic capture of CO₂ in which flue gas is cooled by recuperative heat exchange and an external refrigeration system. As the temperature is lowered, CO₂ freezes directly on the surface of the heat exchanger, in a process referred to as anti-sublimation. The build up of solid CO₂ degrades the performance of the heat exchanger until eventually the flow is switched to a second parallel heat exchanger, while the first exchanger is regenerated to remove the CO₂ (Clodic, 2002; 2005). An alternative cyclic process investigated by Shell and the University of Twente involves feeding flue gas to a pre-refrigerated packed bed (Tuinier, 2010).

Sustainable Energy Solutions (SES), together with GE Global Research, American Air Liquide, Brigham Young University, DONG Energy, CCEMC Canada, US Dept. Of Energy and the Advanced Conversion Technologies Task Force (Wyoming) is developing its Cryogenic Carbon Capture™ process. There two main variants; external cooling loop (ECL) and flue gas compression (FGC), as shown in Figures 4 and 5. In the ECL variant all of the cooling is provided by an external refrigeration loop. In the FGC variant the flue gas is compressed to 5-8 bar and cooled, some solid CO₂ is separated in the first separator and the flue gas is then expanded in a turbine which cools the gas further to enable most of the remaining CO₂ to be recovered in the second separator.

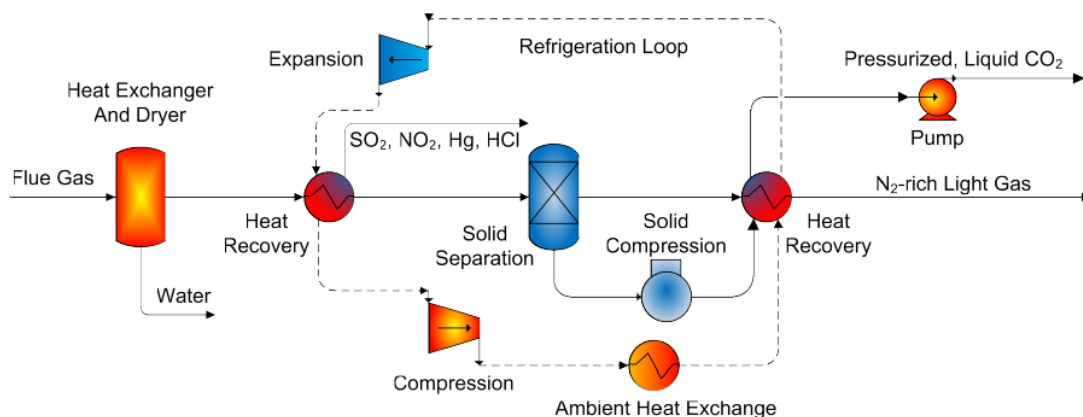


Figure 4 Cryogenic Carbon Capture™ using an external cooling loop (CCC-ECL) (Baxter, 2014)

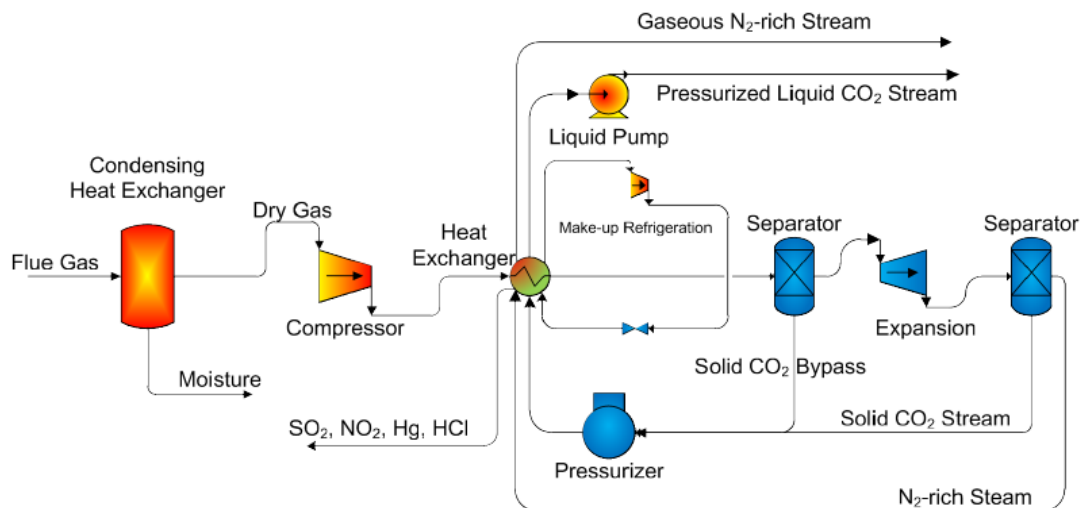


Figure 5 Cryogenic Carbon Capture™ using compressed flue gas (CCC-CFG) (Baxter, 2014)

The critical item in cryogenic capture is a de-sublimating heat exchanger that can produce solidified CO₂ without problems due to fouling. SES has patented three types of de-sublimating heat exchangers (SES, 2016), all of which can operate continuously, the first two of which use a contacting liquid for direct contact heat transfer and the third of which uses cooling rods.

- The bubbling de-sublimating heat exchanger (bubbler) uses a contacting liquid for direct contact heat transfer. It is used in the small pilot demonstrations of the CCC-ECL and CCC-CFG processes. Each bubbling exchanger regularly captures 95–99% of the entering CO₂ and is reported to be capable of continuous carbon capture without any fouling.
- The spray tower is similar to the bubbler, but is more suitable for larger pilot and full scale installations. CO₂ in the gas de-sublimates on the droplet surface in the counter-current flow and is then separated in a settler or barrier filter. Small spray towers have been tested successfully in SES' lab.
- The fluidized bed de-sublimating heat exchanger uses cooling rods. It is reported that it could potentially be the most efficient of the three types of de-sublimating heat exchangers, especially at the full scale but size constraints have prevented SES' small-scale prototypes from reaching the same performance as the other two heat exchangers. However, its potential benefits at full scale, including a high heat exchange capability for its size, make it a good candidate for further development and testing.

The contacting liquid used in the first two types of exchangers is generally thought to be a hydrocarbon mixture but can include any liquid that is environmentally benign, that has a low viscosity at low temperatures and a low vapour pressure to minimise losses in the CO₂ product and treated flue gas (Jensen, 2015a; 2015b). Information on losses of contacting liquid currently appears to be not published.

4.1.2 Energy requirement and costs

The energy consumption for cryogenic separation processes critically depends on the amount of cold energy recovered by heat exchange between hot and cold flue-gas and CO₂ and the efficiency of the refrigeration cycles. The former is limited by the temperature approach which is used and there is a trade-off between energy consumption and heat exchange area, and hence capital cost. An

advantage of cryogenic processes is that they capture CO₂ as a solid which can be pressurised and converted to high pressure liquid CO₂, thereby avoiding the need for energy intensive gaseous CO₂ compression.

The energy consumption for cryogenic CO₂ capture is reported to be significantly lower than that of MEA scrubbing. SES indicates an efficiency improvement of around 5-7 percentage points compared to NETL's Baseline MEA scrubbing plant, which has an efficiency penalty for CO₂ capture of 10.9 percentage points (Baxter, 2016). SES' data are in broad agreement with another study (Clodic, 2005) which shows an energy efficiency reduction for cryogenic capture of 3.8-7.3 percentage points. Another study (Schach, 2011) reports an efficiency penalty for cryogenic capture of 10.7 percentage points, which is lower than the 12.5 percentage point penalty for MEA scrubbing reported in that publication but it is higher than the efficiency penalty of proprietary amines, such as Cansolv, as reported in NETL's latest Rev.3 Baseline study (NETL, 2015).

The energy consumption of cryogenic capture depends strongly on the CO₂ concentration of the feed gas. The energy consumption per tonne of CO₂ captured for gas containing 4% CO₂ is reported to be about 80% higher than for gas containing 14% CO₂ (Clodic, 2005), or 125% higher (Jensen, 2015b). The increase in energy consumption at low CO₂ concentrations is greater than for amine scrubbing. This indicates that cryogenic capture may be less attractive for plants with relatively low CO₂ concentrations, such as gas turbine combined cycle plants, where the CO₂ concentration is around 4%. However, if the gas fired plant uses LNG, the ability to use the cold from LNG re-gasification for cryogenic CO₂ capture may be a potentially attractive synergy.

SES estimates that the reduction in the cost of electricity from use of Cryogenic Carbon Capture™ in a coal fired power plant is around 16-20% compared to MEA scrubbing, rising to about 33% with increased integration (Baxter, 2016; Jensen, 2015b).

In contrast, in another study (Schach, 2011) the equipment cost for a cryogenic capture process that is similar to the cyclic process researched by Clodic is reported to be 2.58 times higher than that of MEA scrubbing and the cost of CO₂ avoided is 46% higher.

4.1.3 Development status and TRL

SES has tested its technology over several months in a 1t/d CO₂ skid on a slipstream of a power plant in Wyoming. Over 90% CO₂ capture and almost complete NO capture has been demonstrated (Baxter, 2016). This qualifies the technology as TRL 5. The next development stage that is proposed is a 100t/d, 5 MW_e pilot plant which would be installed semi-permanently at a host site. Laboratory scale component tests of a cyclic process have been performed (Clodic, 2005) and this technology is assessed as TRL 3. Significant issues for cryogenic capture are handling and pressurisation of low temperature solid CO₂, avoiding formation of blockages and achieving good energy integration.

Although cryogenic separation of CO₂ from flue is at an early stage of development, cryogenic separation from natural gas is a commercially available technology, although the technology is substantially different to flue gas separation. CO₂ solidifies under certain conditions during separation from natural gas and this is permitted to happen in some separation processes. The leading example is ExxonMobil's Controlled Freeze Zone™ process which was operated at a 400,000 standard m³/day commercial demonstration plant at the Shute Creek Treatment Facility in La Barge, Wyoming (Kelley, 2011).

As mentioned at the start of section 4, cryogenic separation of CO₂ from hydrogen-rich gas (CRYOCAP™ process) is also being demonstrated at an industrial scale. Although there may be some transferable learning from demonstration of processes for cryogenic separation of CO₂ from natural gas and hydrogen, flue gas separation processes were judged to be sufficiently different to require their own TRL status.

4.2 Supersonic inertial separation

4.2.1 Process descriptions

Orbital ATK and ACEnT Laboratories are developing an inertial CO₂ extraction system (ICES) in which coal-fired flue gas is compressed and directed to a converging-diverging nozzle where it is expanded to supersonic velocities. The process of aerodynamic expansion to high velocity results in the conversion of potential energy contained in the form of pressure and temperature into kinetic energy. The rapid temperature and pressure decrease produced by this conversion results in the desublimation of CO₂ as well as the condensation of other undesirable constituents of the flue gas. The high density of the solid phase allows for inertial separation by centrifugal forces induced by flow path curvature, as shown in Figure 6. The solid CO₂ separated from the flue gas duct is further concentrated in a dry ice cyclone. Slip gas from the cyclone is recirculated back to the flue gas duct. Large commercial plants would consist of multiple ICES units, for example a 545MW power plant would require twelve full scale ICES nozzles.

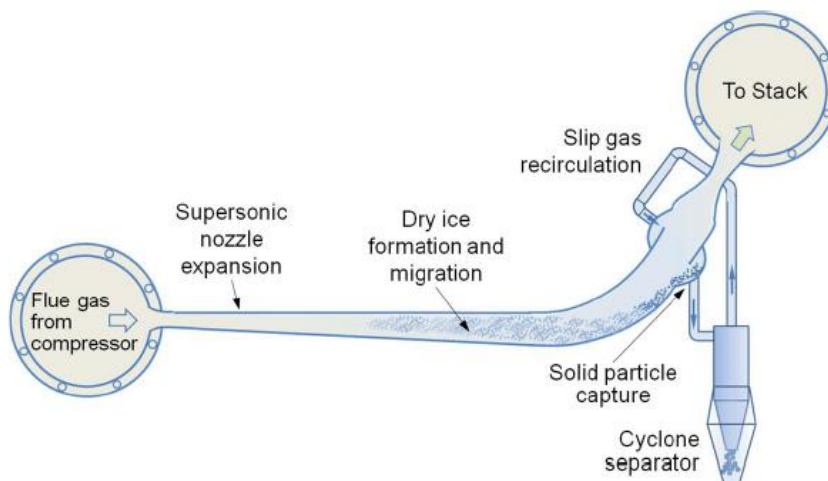


Figure 6 ICES unit schematic (Orbital ATK, 2013)

The key advantages of the technology are reported to be that it has no moving parts (apart from the upstream flue gas compressor), it requires no chemicals, additives or consumable media, it involves inexpensive construction, and it has a small footprint (approximately 30 percent of the size of an equivalent amine system). The main development challenge is to ensure particles grow 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 capture duct. A combination of test data and detailed modelling led to the conclusion that solid media (e.g. CO₂) seeding is the most viable path to 90%+ capture by causing flue gas CO₂ to condense on particles that are already >2.5µm. However, the energy needed to accelerate added particles to high speed has been found to be significant. The process configuration has recently been changed to include pre-cooling of the flue gas using the separated solid CO₂ as a

cold sink. Subsonic condensation of trace water or small quantities of CO₂ could produce larger particles which provide in-situ seeding. Other challenges include minimisation of “slip gas” removed with the solid CO₂, processing the solid CO₂, optimisation of the flowpath pressure recovery, and achieving acceptable CO₂ purity. The supersonic cryogenic process could also in principle be used to separate CO₂ from the flue gas of natural gas combined cycle plants, but it would appear that the formation and separation of CO₂ particles from a dilute gas stream would be more challenging and the energy consumption would be greater due to the higher volume of flue gas.

4.2.2 Energy requirement and costs

A preliminary techno-economic analysis was carried out by Worley Parsons in 2013. The power plant efficiency penalty for capture was predicted to be 4.8 percentage points (HHV basis), compared to 10.9% for a reference plant using MEA scrubbing, i.e. a 6 percentage point advantage. The increase in the cost of electricity due to CO₂ capture was estimated to be 42% compared to 77% for MEA scrubbing (Castrogiovanni, 2016). The cost of electricity would therefore be 20% lower than for MEA scrubbing. The development project has however subsequently shown that the flue gas will need to be compressed by a higher pressure ratio; 5-8 compared to the 2.5 that was assumed for the techno-economic assessment (Castrogiovanni, 2016). As most of the energy consumption and a major part of the cost of the process will be for flue gas compression, the doubling of the compressor power will greatly reduce the advantages of the process. The efficiency advantage compared to MEA may therefore be only around 1-2 percentage points. As well as the additional compression, the increased complexity due to seeding etc. is also likely to increase costs. The electricity cost advantage compared to MEA is highly uncertain but it is speculated here that it may be of the order of 10%. An updated techno-economic analysis is being carried out towards the end of a DOE funded project, which will provide more definitive data.

An assessment of the supersonic capture process applied to NGCC flue gas has shown a 9 percentage point energy penalty for capture, 1 percentage point greater than MEA scrubbing, and a 9% higher cost of CO₂ avoided (Forsyth, 2016).

4.2.3 Development status and TRL

Orbital ATK, ACEnT Laboratories, the Electric Power Research Institute and Ohio State University have a NETL-funded project that is scheduled to complete at the end of September 2017. >50% capture was reported in mid-2015 to have been achieved in several short tests (Balepin, 2015) but ≥90% capture is normally a requirement for commercial capture processes. The technology readiness level is assessed as being at TRL 3 but significant improvement in system performance is required in future.

5. BI-PHASIC SOLVENTS

Research and development is being undertaken on various post combustion capture processes in which there is a change of phase of the CO₂ capture solvent between the absorption and regeneration stages. These include processes in which the CO₂-laden liquid solvent separates into two liquid phases (a CO₂-lean and a CO₂-rich phase), and processes which employ a liquid solvent that becomes a solid when it reacts with CO₂. This section of the report focuses on these two classes of process. Processes that involve potassium carbonate scrubbing and precipitation are discussed in Section 6 on carbonate scrubbing processes.

5.1 Bi-phasic liquid-liquid processes

5.1.1 Process descriptions

A leading example of liquid-liquid bi-phasic solvent processes is IFP's DMX™ process, a simplified flowsheet of which is given in Figure 7. This process is based on a particular combination of solvents which form, for specific CO₂ loading or temperature conditions, two immiscible liquid phases which have different densities and different CO₂ loadings. The heavier phase has a high CO₂ loading while the lighter phase has a low loading or is almost free of CO₂. The two phases are separated in a decanter and only the heavier phase is fed to the regenerator. The lighter phase is mixed with the regenerated solvent coming from the stripper before being fed into the absorber.

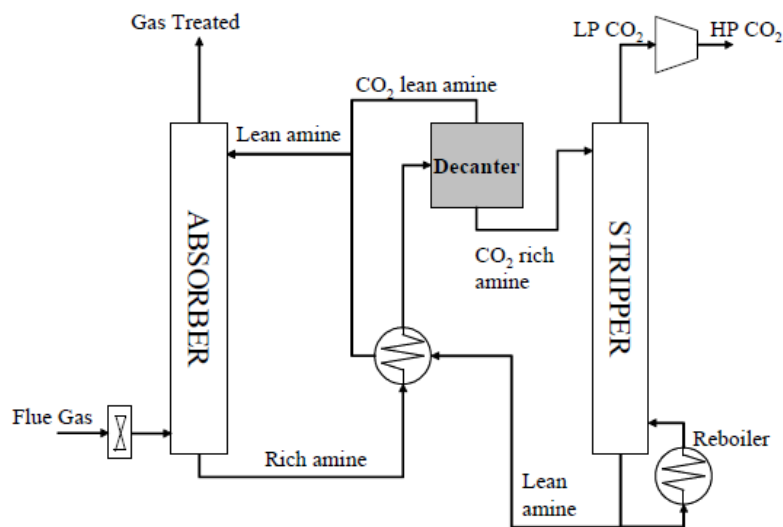


Figure 7 DMX™ bi-phasic liquid process (Raynal, 2011)

Several solvents have been studied by IFP. Development has tended to focus on a solvent called DMX-1 which has a higher cyclic capacity (the difference between the CO₂ content of the rich and lean solvent) than an aqueous solution of MEA, mainly due to a low lean solvent loading. The heat of absorption (around 60 kJ mol⁻¹) is lower than that of MEA (around 85 kJ mol⁻¹). In addition, less stripping is required for solvent regeneration which has a direct impact on the overall heat consumption for regeneration.

It is important to achieve adequate separation of the phases in the decanter in a reasonable time and laboratory tests indicate that this can be achieved in a few minutes. It is difficult to reproduce at a laboratory scale the degradation that occurs in industrial plants but laboratory tests have shown that the DMX-1 solvent has low rates of degradation and it is expected that it would be possible to regenerate the solvent at a higher temperature. Another important issue for CO₂ scrubbers is corrosion. MEA plants have to use corrosion resistant alloys or use corrosion inhibitors but the DMX-1 solvent is substantially less corrosive, which should result in cost savings.

5.1.2 Energy requirement and costs

It is reported that the reboiler heat duty in IFP's DMX™ process could be less than 2.3GJ/t CO₂, although a higher duty of 2.5GJ/t is a more economically optimum value due to lower capex (Raynal, 2014). This is substantially lower than that of a generic MEA scrubber. In the latest assessment carried out by IFP and the Technical University of Hamburg (Broutin, 2016) the energy efficiency

penalty of the DMX™ process in a coal fired power plant is 9.3 percent, i.e. about 1 percentage point lower than MEA scrubbing with lean vapour compression (LVC) and 2 percentage points lower than MEA scrubbing without LVC. The CAPEX of DMX™ plants is predicted to be slightly lower than MEA plants. The increase in the levelised cost of electricity for DMX™ plants is estimated to be 47-50%, compared to 59-62% for MEA plants. This corresponds to the DMX plant having a 7% lower LCOE than an MEA plant.

The iCAP project (EU 7th Framework programme) researched biphasic liquid CO₂ capture, including laboratory scale pilot plant tests. A regeneration heat requirement below 2.4MJ/kg CO₂ captured was achieved experimentally and down to 2 MJ/kg by simulation (ICAP, 2015). An analysis of the efficiency of a power plant using a biphasic liquid process based on a blend of two amines; a tertiary amine DEEA (diethylaminoethanol) and a diamine MAPA (N-methyl-1,3-propanediamine) has been reported by Hamburg University and the Norwegian University of Science and Technology (Liebenthal, 2013). The efficiency penalty for CO₂ capture in a greenfield power plant was estimated to be 5.9% points for the two phase solvent, compared to 9.5% points for MEA. The efficiency improvement is due to a lower desorber heat consumption and a lower CO₂ compressor power which results from the use of a higher desorber pressure.

Experimental results and thermodynamic calculations for other biphasic liquid solvents have indicated regeneration energy consumptions of less than 2.0 GJ/t CO₂ (Zhang, 2013).

5.1.3 Development status and TRL

The DMX™ process is currently at the laboratory scale. The basic concept appears to be proven, the next stage will be pilot plant validation. It was intended that the DMX™ process would be demonstrated as part of the Octavius EU 7th Framework project. This would have been at an existing 2.25t/h CO₂ post combustion capture pilot plant at Enel's coal fired power plant at Brindisi in Italy in 2015-2016, or in a dedicated skid mounted unit. It was however decided not to proceed due to higher than expected costs (Raynal, 2014). The DMX™ process is judged to be at TRL 4.

5.2 Bi-phasic liquid-solid processes

5.2.1 Process descriptions

An alternative to producing a concentrated CO₂-rich liquid phase is to separate a CO₂-rich solid phase. Some such processes involve the use of potassium carbonate solvent and these are discussed separately in Section 6. Leading developers of other such processes include GE and TNO. An outline schematic of GE's process is given in Figure 8. Flue gas from a direct contact water cooler is contacted with lean sorbent in a spray absorber. CO₂-laden solid sorbent from the absorber and cyclone is then pressurised and fed to a desorber, from which lean sorbent is fed back to the absorber. The process has the advantage of a low energy consumption but it has the disadvantage of involving handling and pressurisation of solids, which is more difficult than movement of liquids.

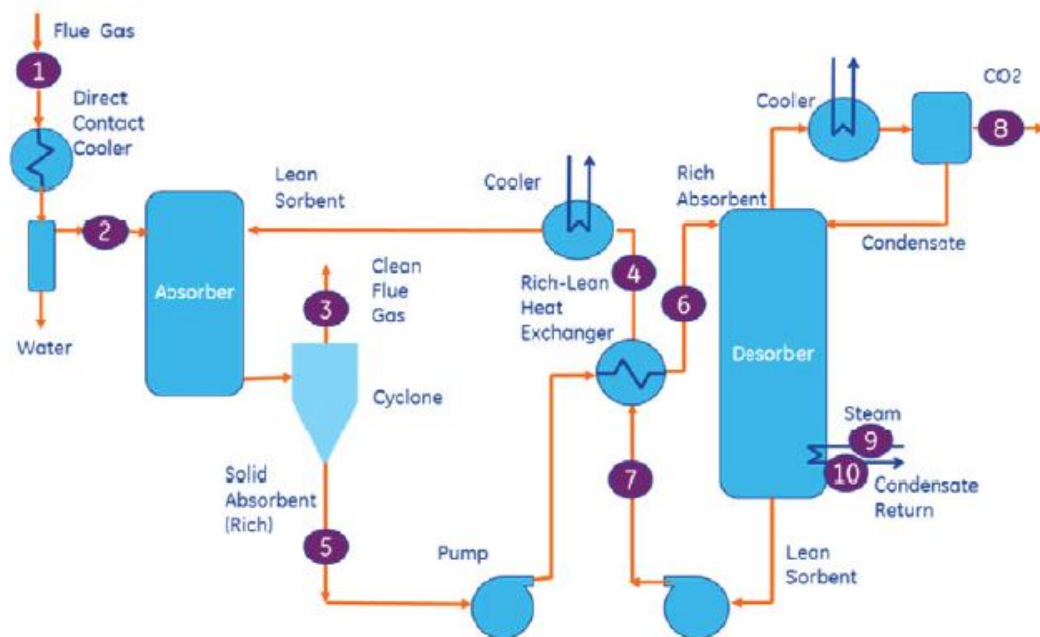


Figure 8 GE phase changing absorbent process (Gonzalez-Salazar, 2012)

GE's process is based on the use of amino silicone solvents. Several solvents were identified which form a powder when they combine with CO₂ but some of them formed solids that would be difficult to handle when using flue gas that contains water. A material (GAP-0) has been selected that has an acceptable CO₂ loading (>11wt% between absorption and desorption), low vapour pressure compared to MEA, fast reaction rate and thermal stability. There are various options for handling and pressurisation of the solid CO₂-laden sorbent, including lock hoppers, screw conveyors, piston pumps and GE's Posimetric™ pump. The choice is contingent on the characteristics of the solid, such as density, shape, cohesiveness, moisture content and thermal stability.

TNO has undertaken research on a precipitating amino acid process called DECAB as part of the EU funded CESAR project (TNO, 2011) and the Dutch CATO-2 programme (Sanchez-Fernandez, 2014). Precipitation is achieved using a spray column.

5.2.2 Energy requirement and costs

In 2012 GE published an evaluation of their process for three different flue gas CO₂ concentrations; 4% (NGCC), 8% and 13% (coal fired plant) and compared the results to an MEA baseline (Gonzalez-Salazar, 2012). The specific equivalent work for CO₂ capture and compression (MJ_e/kg CO₂) using the GE process in greenfield power plants was estimated to be 34% lower than for MEA for 13% CO₂ flue gas and 23% lower for 4% CO₂ flue gas. A 34% reduction corresponds to 3-4 percentage points of power generation efficiency.

The cost per tonne of CO₂ was recently reported to be \$45-50 compared to \$66 for NETL's baseline MEA scrubbing plant, i.e. up to a 30% reduction (Westendorf, 2016). This corresponds to about a 13% reduction in the cost of electricity.

TNO's DECAB process was reported to have the potential for up to 30 to 40% lower energy consumption than MEA, a significant CAPEX reduction and a total capture cost reduction of 30% compared to MEA (TNO, 2011). These estimates are in line with those of GE's process.

5.2.3 Development status and TRL

GE's process is being developed at bench scale under a DOE funded project that is scheduled to complete at the end of 2016 (Westendorf, 2016). The process is rated as TRL 4. The main development issues are related to solids handling and fouling and sorbent performance, stability, cost, corrosion etc.

6. POTASSIUM CARBONATE SCRUBBING

The Benfield™ hot potassium carbonate scrubbing process was developed in the 1950s for separation of CO₂ from synthesis gas. The process has been further developed, for example by adding rate promoters and using improved packings, and several hundred plants are in operation. Potassium carbonate has several advantages compared to amines such as a low solvent cost, low volatility, lack of degradation and production of potentially harmful compounds and relatively low energy consumption. A disadvantage is that it has relatively slow reaction kinetics, which has made it unattractive for scrubbing CO₂ from atmospheric pressure flue gas. The rate of absorption can be increased by use of promoters such as DEA or piperazine (Hu, 2016). Use of piperazine promoted potassium carbonate instead of MEA for post combustion CO₂ capture at a coal fired power plant is reported to result in a 1 percentage point lower efficiency and an 8 percent higher cost of electricity (Oexmann, 2009). Techniques that are being researched to improve the competitiveness of potassium carbonate scrubbing for capture of CO₂ from flue gas are operation at elevated pressure and precipitation. These techniques are described below. Another technique, not discussed here, is the use of enzymes to enhanced CO₂ capture by carbonate or other solvents.

6.1 Potassium carbonate scrubbing at elevated pressure

6.1.1 Process description

The Sargas process uses hot potassium carbonate scrubbing to capture CO₂ from flue gas at elevated pressures. Two process variants have been proposed, a coal or biomass-fired variant based on pressurised fluidised bed combustion (PFBC) and a gas-fired variant based on a version of GE's LMS100 gas turbine, divided into two parts. In the coal-fired variant, flue gas from a pressurised combustor is cooled, cleaned and fed to a carbonate scrubber before being reheated by heat exchange with the hot gas from the combustor and then expanded to atmospheric pressure in a turbine. A diagram of the gas-fired variant is shown in Figure 9.

Gas from the first expansion stages of a gas turbine is fed to a gas fired steam boiler where more fuel gas is combusted. The flue gas at about 8bar is then cooled, fed to a carbonate scrubber, reheated and expanded to atmospheric pressure in a turbine. A more in-depth discussion of the Sargas process is included in an earlier study for ETI (Davison, 2012).

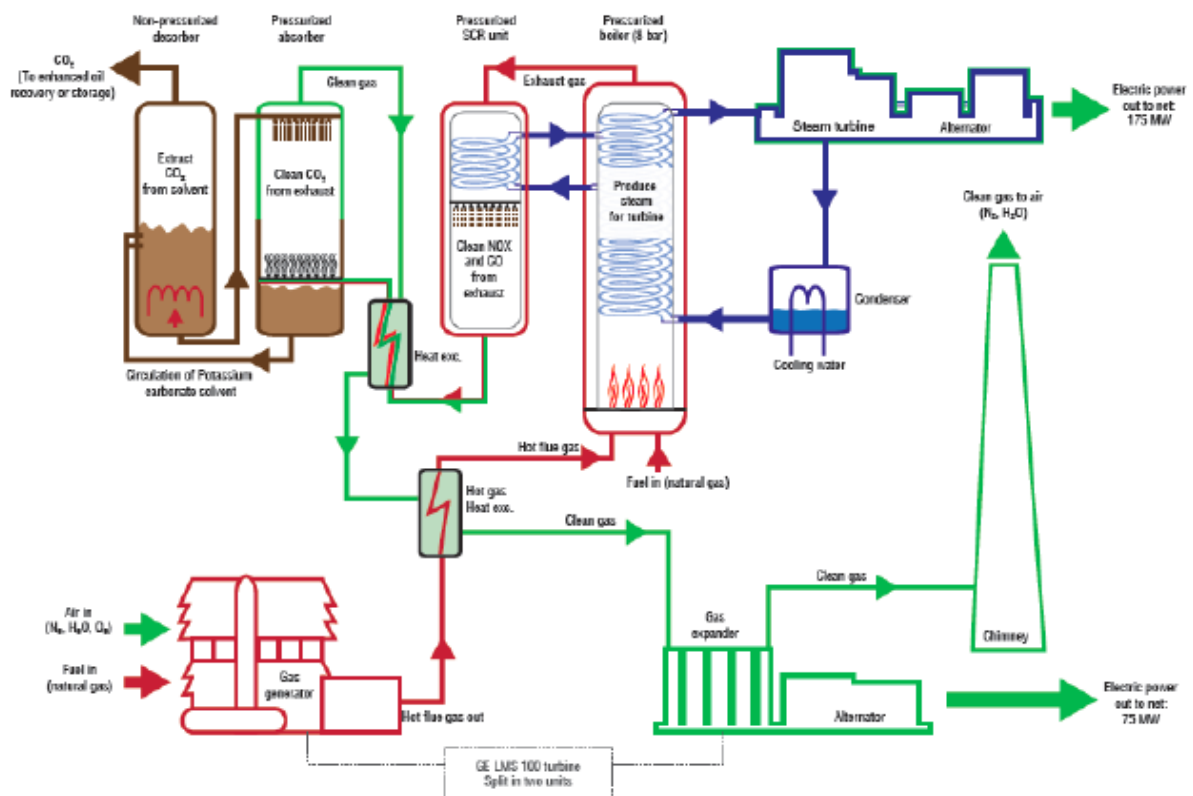


Figure 9 Gas fired Sargas process with elevated pressure CO₂ capture (Sargas, 2014)

6.1.2 Energy requirement and costs

The gas-fired Sargas process is reported by its developer to have an efficiency of up to 48% (LHV). The process is a “fully fired” combined cycle in which only part of the fuel is fed to the high efficiency gas turbine and the rest is combusted to produce heat to generate steam for a steam cycle. Full firing normally reduces the efficiency of combined cycle plants, which will offset efficiency benefits of higher pressure CO₂ capture. An independent assessment reports an efficiency of 40% (LHV) and a cost of CO₂ avoided that is 16% higher than MEA scrubbing (Forsyth, 2016).

6.1.3 Development status and TRL

As part of the development of the Sargas process, a pressurised potassium carbonate scrubbing pilot plant was operated in 2007-8 using a side-stream of gas from an 80MW_e PFBC plant at Vartan, Sweden. The plant processed 60 kg/h of flue gas (about 0.04 MW_{th}) and captured over 95% of the CO₂ (Doyle, 2007). 98% capture is reported to be feasible but the optimum would depend on environment requirements and economics. This qualifies pressurised potassium carbonate scrubbing of coal-derived flue gas as TRL 5. A move directly to commercial scale was envisaged. Sargas executed a production licence agreement with Daewoo Shipbuilding and Marine Engineering (DSME) and a commercial collaboration agreement with GE. A natural gas-fired Sargas plant at Point Comfort, Texas plant which would have generated nominally 250MW_e and captured 0.8Mt/y of CO₂ for EOR had been in the definition phase (Sargas, 2014) but it is reported that the Sargas company collapsed in 2015 (Tradewindsnews, 2015).

6.2 Potassium carbonate scrubbing with precipitation

6.2.1 Process description

Various organisations, including Shell, the Cooperative Research Centre for Greenhouse Gas Technologies (CO2CRC) and the University of Illinois have worked on developing scrubbing processes that involve precipitation of potassium bicarbonate. A key benefit of such processes is the potential for a lower energy consumption. All of the main contributions to the energy consumption of solvent scrubbing processes (the heat of reaction, the sensible heat, the stripping heat and the compression work) are lower than for MEA scrubbing. An example of such a process, the UNO Mk3 process developed by CO2CRC, is shown in Figure 10.

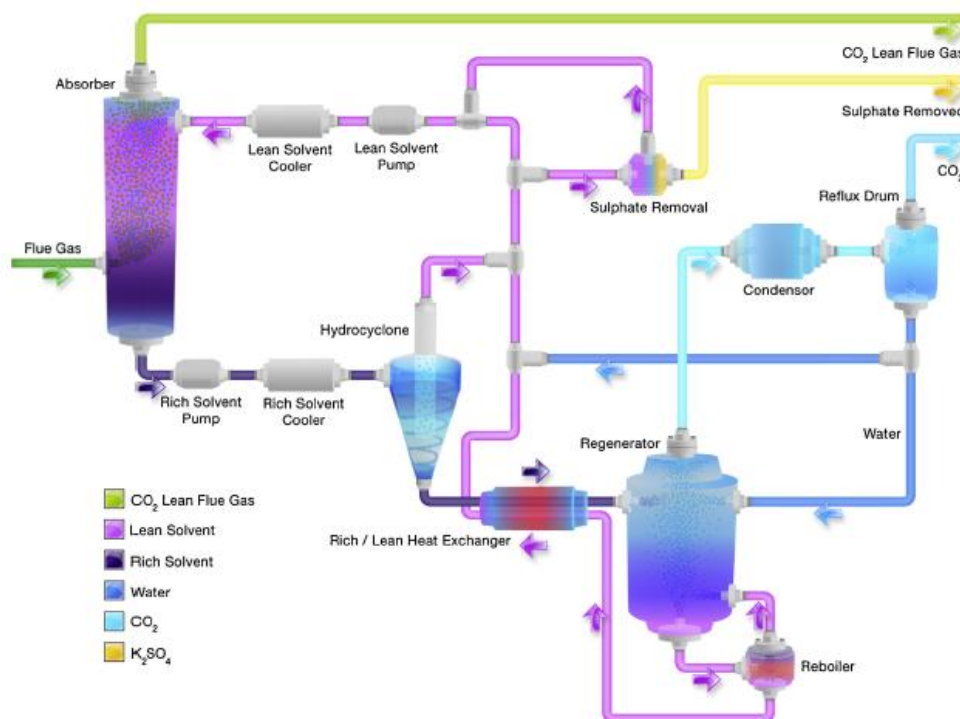


Figure 10 Simplified diagram of the UNO Mk3 process (Anderson, 2014)

In the absorber column K_2CO_3 reacts with CO_2 to form $KHCO_3$. Precipitation will occur once the concentration reaches the solubility limit. The concentration of solid $KHCO_3$ is increased by cooling prior to separation in a hydrocyclone. The bicarbonate slurry from the hydrocyclone is fed to the regenerator where it is heated and CO_2 is recovered. The regenerator can be operated at elevated pressure, which minimises the CO_2 compressor power requirement.

As well as CO_2 , K_2CO_3 also reacts with SO_x and NO_x in flue gas, producing K_2SO_4 and KNO_3 . This can avoid the need for an upstream FGD process but removing sulphate and nitrate from the carbonate solvent adds to the process complexity.

6.2.2 Energy requirement and costs

The performance and costs of retrofitting UNO Mk3 CO_2 capture to black coal power plants has been estimated (Pandit, 2014a). Capturing 90% of the CO_2 reduced the efficiency of power generation by 6.1-7.6 percentage points, depending on the level of heat integration and increased the LCOE by 70%. The LCOE of a plant with UNO Mk3 was estimated to be 30% lower than that of a plant with

MEA scrubbing and 24% lower than that of a plant with “state of the art” amine scrubbing, but this is compared to a relatively high baseline MEA plant cost and it takes into account a substantial revenue from sale of K_2SO_4 and KNO_3 by-products that may not apply if the process was applied on the very large scale required for global climate change mitigation. Application of the UNO Mk3 process at natural gas fired power plants was also assessed (Pandit, 2014b). The efficiency penalty for CO_2 capture was estimated to be 8.9 percentage points, 2 percentage points lower than MEA scrubbing. Including turbine exhaust gas recycle (EGR) and energy integration increased the efficiency of a power plant with UNO Mk3 scrubbing by 2.2 percentage points. The LCOE of a UNO Mk3 plant without EGR and heat integration was 14% lower than that of a plant with MEA scrubbing.

The US DOE has funded development of the University of Illinois’ Hot-CAP carbonate scrubbing process with precipitation. A techno-economic assessment compared subcritical coal-fired power plants with MEA scrubbing and the Hot-CAP process (University of Illinois, 2014). The power generation efficiency of the Hot-CAP plant was 29.0% (HHV basis), which is 7.8 percentage points lower than NETL’s baseline power plant without capture and 2.8 percentage points higher than NETL’s subcritical baseline plant with MEA scrubbing. The LCOE of the power plant with Hot-CAP scrubbing was 60% higher than the plant without capture and 13.5% lower than the plant with MEA scrubbing. Data for the Hot-CAP process is presented in Table 1 in the Executive Summary because it does not rely on high revenues from sale of by-products and it is based on the NETL baseline plants which are used in the assessments of some of the other capture processes.

6.2.3 Development status and TRL

The UNO Mk3 process has been operated in a laboratory pilot plant using synthetic flue gas. A pilot plant processing 70 to 350kg/h of flue gas from a Victorian brown coal fired power plant has operated for over 1000 hours (Anderson, 2014). 50% capture was achieved in a limited height absorber. The process is classified as TRL 5, with the caveat that a higher capture rate needs to be achieved. The next phase will be trials with a full height absorber to increase the CO_2 capture to 90%, the trialling of a high rate promoter which achieved favourable results in laboratory tests and validation and optimisation of simulation models (Anderson, 2014).

Proof of concept tests of the Hot-CAP process at a component level have been carried out in the laboratory. The process is classified as TRL 3.

Shell has undertaken bench scale pilot plant tests of a precipitating potassium carbonate process (Moene, 2013), indicating TRL 4. The CO_2 vapour pressure of lean solvent entering the absorber was reported to be low enough to in principle provide sufficient driving force at the top of the absorber column for 90% removal of CO_2 from flue gas containing 4% CO_2 .

7. REFERENCES

- Air Liquide, 2015. World premier: Air Liquide inaugurates its CO₂ cold capture system CRYOCAP™. Press release, Paris, 5th Nov. 2015. <https://www.airliquide.com/file/33766/download?token=xIHsppl8>
- Anderson, C. et. al., 2014. Recent developments in the UNO Mk3 process – a low cost environmentally benign precipitating process for CO₂ capture. *Energy Procedia* 63 (2014) 1773-1780.
- Augustine, A., Gagliano, R., Fu, S., Hasse, D., Kulkarni, S., Kratzer, D., Bennett, M., Gauthier, J-M., 2016. Project review: bench scale testing of next generation hollow fiber membrane modules. NETL CO₂ capture technology meeting, Aug. 10, 2016.
- Balepin, V., Castrogiovanni, A., Robertson, A., Tyll, J., 2015. Supersonic post-combustion inertial CO₂ extraction system – bench scale project status update. NETL CO₂ capture technology meeting, Pittsburgh, 24 June 2015.
- Baxter, L., 2014. Skid-scale Cryogenic Carbon Capture™ demonstration. Orem, UT, 21 Aug. 2014.
- Baxter, L., Baxter, A., Bence, C., Frankman, D., Hoeger, C., Sayre, A., Stitt, K., Chamberlain, S., 2016. Cryogenic carbon capture. CO₂ Summit II: Technologies and Opportunities, 4-11-2016. http://dc.engconfintl.org/co2_summit2/12
- Broutin, P., Briot, P., Ehlers, S., Kather, A., 2016. Benchmarking of the DMX™ process. GHGT-13, Lausanne, Switzerland, 13-18 Nov. 2016.
- Campanari, S., Chiesa, P., Manzolini, G., Bedogni, S., 2014. Economic analysis of CO₂ capture from natural gas combined cycles using molten carbonate fuel cells. *Applied Energy* 130 (2014) 562-573.
- Castrogiovanni, A., Balepin, V., Robertson, A., Calayag, B., 2016. Supersonic post-combustion inertial CO₂ extraction system – bench scale project status update. NETL CO₂ capture technology meeting, Pittsburgh, 10 August 2016.
- Chaubey, T., 2016. CO₂ capture by cold membrane operation with actual power plant flue gas. NETL CO₂ capture technology meeting, Aug. 10, 2016.
- Clodic, D., Younes, M., 2002. A new method for CO₂ capture: frosting CO₂ at atmospheric pressure. Sixth International Conference on Greenhouse Gas Control Technologies GHGT6, Kyoto, Japan, 1-4 October 2002, 155-160.
- Clodic, D., EL Hitti, R., Younes, M., Bill, A., Casier, F., 2005. CO₂ capture by anti-sublimation: Thermo-economic process evaluation. Paper presented at the 4th Annual Conference on Carbon Capture & Sequestration, May 2-5, 2005, Alexandria (VA), USA.
- Davison, J., 2012. An assessment of the performance and costs of new CCS processes. Report prepared for ETI, Dec. 2012.
- DOE, 2015. DOE selects eight projects to receive funding for reducing the cost of CO₂ capture and compression. www.energy.gov/fe/articles/doe-selects-eight-projects-receive-funding-reducing-cost-co2-capture-and-compression
- Doyle, A., 2007. Clean coal test traps 95% carbon – Norway firm. Reuters, 16 Nov. 2007.

ETI, 2016. Reducing the cost of CCS, developments in capture plant technology, an insight report from the ETI. Energy Technologies Institute, Loughborough, UK, 2016.

ExxonMobil, 2016. ExxonMobil and Fuel Cell Energy Inc. pursue novel technology in carbon capture, May 5, 2016. <http://news.exxonmobil.com/press-release/exxonmobil-and-fuelcell-energy-inc-pursue-novel-technology-carbon-capture>

Forsyth, J., Lodge, S., Consonni, S., Di Bona, D., Gatti, M., Martelli, E., Scaccabarozzi, R., Vignano, F., 2016. Evaluation of five alternative CO₂ capture technologies with insights to inform further development. GHGT13 conference, Lausanne, Switzerland, Nov. 2016.

Freeman, B., Bhowan, A., 2011. Assessment of the technology readiness of post-combustion CO₂ capture technologies. Energy Procedia 4 (2011) 1791-1796.

Freeman, B., Hao, P., Baker, R., Kniep, J., Chen, E., Ding, J., Zhang, Y., Rochelle, G., 2014a. Hybrid membrane-absorption CO₂ capture process. Energy Procedia 63 (2014) 605-613.

Freeman, B., 2014b. Capture activities and concepts for hybrid CO₂ capture systems for NGCC applications. Natural gas CCS network, Feb. 11, 2014.

Freeman, B., Kniep, J., Baker, R., Merkel, T., Hao, P., Rochelle, G., Chen, E., Zhang, Y., Ding, J., Sherman, B., 2015. Bench scale development of a hybrid membrane-absorption CO₂ capture process. NETL CO₂ capture technology meeting, August 10, 2016.

Fuel Cells Bulletin, 2016. ExxonMobil, Fuel Cell Energy trial MCFCs in carbon capture. Fuel Cells Bulletin, May 2016, 12-13.

Ghezel-Ayagh, H., 2015. Electrochemical membrane for CO₂ capture and power generation. 2015 NETL CO₂ Capture Technology Meeting, 23 June 2015, Pittsburgh, PA, USA.

Ghezel-Ayagh, H., 2016. Pilot test of novel electrochemical membrane system for carbon dioxide capture and power generation. 2016 NETL CO₂ Capture Technology Meeting, 8-12 August 2016, Pittsburgh, PA, USA.

Gonzalez-Salazar, M., Perry, R., Vippera, R., Hernandez-Nogales, A., Nord, L., Michelassi, V., Shisler, R., Lissianski, V., 2012. Comparison of current and advanced post-combustion CO₂ capture technologies for power plant applications. Energy Procedia 23 (2012) 3-14.

Hu, G., Nicholas, N., Smith, K., Mumford, K., Kentish, S., Stevens, G., 2016. Carbon dioxide absorption into promoted potassium carbonate solutions: a review. Int. J. Greenhouse Gas Control 53 (2016) 28-40.

ICAP, 2015. Final report summary – ICAP innovative CO₂ capture. http://cordis.europa.eu/results/rcn/156228_en.html

Jacobs Consultancy, 2015. Evaluation of integrating a molten carbonate fuel cell (MCFC) with a SAGD facility. www.ai-ees.ca/wp-content/uploads/2016/04/2251_mcfc_integration_evaluation_-_final_report_-_2015-07-30.pdf

Jensen, M., 2015a. Energy process enabled by Cryogenic Carbon Capture. Thesis, Brigham Young University, 2015.

Jensen, M., Russell, C., Bergeson, D., Hoeger, C., Frankman, D., Bence, C., Baxter, L., 2015b. Prediction and validation of external cooling loop cryogenic carbon capture (CCC-ECL) for full-scale coal-fired power plant retrofit. *Int. J. Greenhouse Gas Control* 42 (2015) 200-212.

Jordal, K., Anantharaman, R., 2016. A comparison of post combustion capture technologies for the NGCC. GHGT13 conference, Lausanne, Switzerland, Nov. 2016.

Kelley, B., Valencia, J., Northrop, P., Mart, C., 2011. Controlled Freeze Zone™ for developing sour gas reserves. *Energy Procedia* 4 (2011) 824-829.

Kniep, J., Merkel, T., Watson, B., Westling, E., Farzan, H., Seshadri, P., 2016. Integrated testing of a membrane CO₂ capture process with a coal-fired boiler. NETL CO₂ capture technology review meeting, Aug. 8, 2016.

Liebenthal, U., Pinto, D., Monteiro, J., Svendsen, H., Kather, A., 2013. Overall process analysis and optimization for CO₂ capture from coal fired power plants based on phase change solvents forming two liquid phases. *Energy Procedia* 37 (2013) 1844-1854.

Moene R., Schoon L., van Straelen J., Geuzebroek F., 2013. Precipitating carbonate process for energy efficient post combustion CO₂ capture. *Energy Procedia*, 37 (2013) 1881–1887.

NETL, 2010. Cost and performance baseline for fossil energy plants, volume 1: bituminous coal and natural gas to electricity, revision 2. US Department of Energy, National Energy Technology Laboratory, DOE/NETL-2010/1397, Nov. 2010.

NETL, 2012. Current and future technologies for power generation with post-combustion carbon capture. DOE/NETL-2012/1557, March 16, 2012.

NETL, 2015. Cost and performance baseline for fossil energy plants, volume 1a: bituminous coal (PC) and natural gas to electricity, revision 3. US Department of Energy, National Energy Technology Laboratory, DOE/NETL-2015/1723, July 6, 2015.

Oexmann, J., Kather, A., 2009. Post-combustion CO₂ capture in coal-fired power plants: comparison of integrated chemical absorption processes with piperazine promoted potassium carbonate and MEA. *Energy Procedia* 1 (2009) 799-806.

Orbital ATK, 2013. Supersonic post combustion inertial CO₂ extraction system. Kickoff presentation to NETL, contract #DE-FE0013122, Pittsburgh, Pa, Nov. 14, 2013.

Pandit, J., Harkin, T., Anderson, C., Ho, M., Hooper, B., 2014a. Analysis of a precipitating solvent absorption process for reducing CO₂ emissions from black coal fired power generation. *Int. J. Greenhouse Gas Control* 29 (2014) 50-60.

Pandit, J., Harkin, T., Anderson, C., Ho, M., Wiley, D., Hooper, B., 2014b. CO₂ emission reduction from natural gas power stations using a precipitating solvent absorption process. *Int. J. Greenhouse Gas Control* 28 (2014) 234-247.

Raynal, L., 2011. The DMX™ process: an original solution for lowering the cost of post-combustion carbon capture, *Energy Procedia* 4 (2011) 779-786.

Raynal, L., 2014. Evaluation of the DMX process for industrial pilot demonstration – methodology and results. *Energy Procedia* 63 (2014) 6298-6309.

Rexed, I., della Pietra, M., McPhail, S., Lindbergh, G., Lagergren, C., 2015. Molten carbonate fuel cells for CO₂ separation and segregation by retrofitting existing plants – an analysis of feasible operating windows and first experimental findings. *Int. J. Greenhouse Gas Control* 35 (2015) 120-130.

Sanchez-Fernandez, E., Hefferman, K., van der Ham, L., Linders, M., Goetheer, E., Vlugt, T., 2014. Precipitating amino acid solvents for CO₂ capture – opportunities to reduce costs in post combustion capture. *Energy Procedia* 63 (2014) 727-738.

Sandru, M., Kim, T-K., Capala, W., Huijbers, M., Hagg, M-B., 2013. Pilot scale testing of polymeric membranes for CO₂ capture from coal fired power plants. *Energy Procedia* 37 (2013) 6473-6480.

Sargas, 2014. Delivering the future of clean power generation: a solution for cost competitive, clean and reliable power generation and CO₂ for enhanced oil recovery. Presentation to Wyoming Infrastructure Authority spring conference, May 2014. wyia.org/wp-content/uploads/2014/05/Chris-elrod.pdf

Schach, M-O., Oyarzún, B., Schramm, H., Schneider, R., Repke, K-K., 2011. Feasibility study of CO₂ capture by anti-sublimation. *Energy Procedia* 4 (2011) 1403-1410.

SES, 2016. http://sesinnovation.com/technology/Heat_Exchangers/#desub

Spinelli, M., Romano, M., Consonni, S., Campanari, S., Marchi, M., Cinti, G., 2014. Application of molten carbonate fuel cells in cement plants for CO₂ capture and clean power generation. *Energy Procedia*, 63 (2014) 6517-6526.

Terrien, P., Lockwood, F., Granados, L., Morel, T., 2014. CO₂ capture from H₂ plants: implementation for EOR. *Energy Procedia* 63 (2014) 7861-7866.

TNO, 2011. CESAR D1.2.3 approved DECAB precipitating amino acid - TNO – public summary <http://www.co2cesar.eu/downloadables/Deliverables%20Public%20Summaries/CESAR-D1.2.3-APPROVED-DECAB%20Precipitating%20Amino%20Acid%20-%20TNO%20-%20PUBLIC%20SUMMARY%20-%202011.03.25.pdf>

Tradewindsnews, 2015. <http://www.tradewindsnews.com/weekly/771429/sargas-failure-spurs-lange-to-focus-on-shipowning>

Tuinier, M., van Sint Annaland, M., Kramer, G., Kuipers, J., 2010. Cryogenic CO₂ capture using dynamically operated packed beds. *Chem. Eng. Sci.* 65 (2010) 114-119.

University of Illinois, 2014. Bench-scale development of a hot carbonate absorption process with crystallization-enabled high-pressure stripping for post-combustion CO₂ capture. Final scientific/technical report, project period Jan. 1, 2011 – March 31, 2014, DOE award No: DE-FE0004360, April, 2014.

Wee, J-H, 2014. Carbon dioxide emission reduction using molten carbonate fuel cell systems. *Renewable and Sustainable Energy Reviews* 32 (2014) 178-191.

Westendorf, T., 2016. Bench-scale process for low-cost carbon dioxide (CO₂) capture using a phase-changing absorbent. 2016 NETL capture technology project review meeting, August 10, 2016.

Zhang, J., Qiao, Y., Wang, W., Misch, R., Hussain, K., Agar, D., 2013. Development of an energy-efficient CO₂ capture process using thermomorphic biphasic solvents. *Energy Procedia* 37 (2013) 1254-1261.