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Further Assessment of
Emerging CO₂ Capture
Technologies for the Power
Sector and their Potential to
Reduce Costs

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FURTHER ASSESSMENT OF EMERGING CO₂ CAPTURE TECHNOLOGIES FOR THE POWER SECTOR AND THEIR POTENTIAL TO REDUCE COST

Key Messages

- In 2014, IEAGHG commissioned a study “Assessment of Emerging CO₂ capture technologies and their potential to reduce costs” [1] to assess the technical status, and the potential for cost reduction, of a series of emerging CO₂ capture technologies. The aim of this study is to update the CO₂ capture benchmark technology, to provide an update on the current status of these technologies by measuring their progress in terms of Technology Readiness Level (TRL) and to perform the techno-economic assessment of selected CO₂ capture technologies for fossil-fired power plants.
- Based on available commercial CO₂ capture systems, with enhanced performance, 30w.t.% MEA (Monoethanolamine) -based chemical absorption is no longer regarded as a representative benchmark CO₂ capture technology. A further aim of this study is the adoption of a new benchmark solution which can be used as a reference system in future assessments.
- A PZ(Piperazine)+ AMP(2-amino-2-methyl-1-propanol) solution (40w.t.%, 1:2 Molar ratio) is proposed as the new benchmark.
- The new benchmark solution (PZ+AMP) shows a CO₂ avoidance cost reduction of 22% for coal-fired, and 15% for gas-fired power plants, compared to a 30w.t.% MEA-based system. The reboiler heat duty (heat energy to regenerate the solvent) of the new benchmark is similar to that of current commercial blends.
- Chemical absorption is still leading the list of emerging CO₂ capture technologies as it has reached TRL 9 compared to the lower TRLs of other technologies.
- This study has investigated the progress of several post-combustion systems and shown further technological development is possible. Moreover, oxyfuel turbines are expected to advance in the near future.
- Front-end engineering design (FEED) research studies show that there is significant potential to reduce the Levelised Cost of Electricity (LCOE) in electrochemical separation (fuel-cells). An estimated 30% reduction in the LCOE has been predicted but this claim requires confirmation through large-scale demonstration projects.
- Other capture systems with medium LCOE reduction potential (10%-30%) are based on chemical absorption with water-lean, precipitating or catalysed sorbents, membrane separation, PSA (pressure-swing adsorption), TSA (temperature-swing adsorption), calcium looping (Ca-looping), and cooling and liquefaction. Moreover, pressurized oxyfuel combustion, chemical-looping combustion and SEWGS (sorption-enhanced water-gas shift) are also expected to show some LCOE reduction (<10%).



- The techno-economic review covered Ca-looping, membrane-system (MTR Polaris), Allam cycle, and chemical absorption (using 30w.t.%MEA and 40w.t.% PZ + AMP solution) for gas-fired power plants, and Ca-looping, membrane-system (MTR Polaris), solid sorbent-system (Veloxotherm), liquid-liquid separating system (DMX), and chemical absorption (using 30w.t.%MEA and 40w.t.% PZ+AMP) for coal-fired power plants. Coal-fired and gas-fired power plants without CO₂ capture systems were assessed for comparison.
- The techno-economic assessment shows the impact of regional, financial and economic conditions on the LCOE obtained by the different CO₂ capture technologies applied to gas-fired and coal-fired power plants.
- For coal-fired power plants, the new benchmark solution (40w.t.% PZ + AMP) shows the lowest LCOE, while the Allam cycle would be, economically, the most favourable option for gas-fired power plants. However, in both gas and coal-fired power plants the other CO₂ capture alternatives could be more favourable under specific financial and economic conditions.
- The results from this techno-economic review have been based on information from research literature. Differences in cost-methodologies, including the assessment of contingencies, are explained in detail. Moreover, technologies at different TRLs have been compared which limits the level of confidence that can be placed on the results.
- Based on the results from this study, it is recommended that the most promising technologies should be followed-up, and more detailed cost evaluation studies pursued, together with an evaluation of their extended value within electricity supply, grid distribution and broader decarbonisation goals.

Scope of Work

CSIRO was commissioned by IEAGHG to provide a comprehensive assessment of emerging CO₂ capture technologies for the power sector and their potential to reduce costs. The objectives of this technical study were:

- to update the CO₂ capture benchmark technology and its enhancement over the 30w.t.% MEA-based chemical absorption
- to review the CO₂ capture technologies, their current status and trajectory
- to assess the potential of emerging CO₂ capture systems to reduce costs (LCOE) and identify risks and barriers for those on the path to TRL 9
- to assess techno-economically a number of selected CO₂ capture technologies for coal and gas-fired power plants.



Findings of the Study

This study was divided in three tasks, which are described below:

1. Update on the CO₂ capture benchmark technology

The objective of this task was to reproduce, with an open-source solution, the current commercial solvents-based systems with enhanced performance over the 30w.t.%MEA solution. The key parameter to measure this improvement was the reboiler duty, calculated through modelling a 90% capture rate system. The selected solution was a blend of 40w.t.% PZ+AMP (1:2 molar ratio), with an advanced process configuration (absorber intercooling and rich flow).

Table 1 Overview of techno-economic assessment for two types of power plants without (W/O) post-combustion capture (PCC), with capture via 30w.t.% MEA, and with capture using a 40w.t.% PZ/AMP blend.

	Ultra-supercritical coal-fired power plant			Natural-gas combined-cycle power plant		
	W/O PCC	MEA	PZ/AMP	W/O PCC	MEA	PZ/AMP
Technical performance						
Gross power output (MW)	900	900	900	890	890	890
Auxiliary power (MW)	83	266.1	215.6	12	161.8	128.2
Net power output (MW)	817	633.9	684.4	878	728.2	761.9
Net plant higher heating value efficiency (%)	42.5	32.97	35.59	52.66	43.91	45.94
Net plant lower heating value efficiency (%)	44.4	34.48	37.23	58.25	48.57	50.82
CO ₂ generation (t/h)	604	604	603.3	310	310	310
CO ₂ emission (t/h)	604	61	59.1	310	31	31
CO ₂ emission (t/MWh)	0.739	0.095	0.084	0.353	0.042	0.040
CO ₂ capture (t/h)	0	543	544	0	279	279
Equivalent energy consumption (MWh/tCO ₂)	–	0.337	0.244	–	0.506	0.423
Economic performance						
Total capital requirement (million €)	1342.8	1681.1	1659.5	835.7	1172.8	1166.3
Specific capital requirement (€/kW)	1647	2654	2424	939	1611	1531
Fixed operations & maintenance (O&M) (million €)	37.7	46.3	45.9	29.2	39.7	39.5
Variable O&M (million €)	7.54	20.1	17.8	3.41	11.9	9.1
LCOE (€/MWh)	51.6	87.0	79.5	52.9	77.6	73.8
CO ₂ avoided cost (€/tCO ₂)	–	55.0	42.8	–	79.3	67.1

W/O PCC = without post-combustion capture

As observed in Table 1, using the new benchmark solution, the CO₂ avoidance cost is reduced by 22% and 15% in coal and gas-fired plants respectively.



2. Review of the TRL, trajectory and potential to reduce LCOE of CO₂ capture technologies

Post-combustion is the CO₂ capture arrangement that has advanced the most in recent years. In addition, amino acid and other mixed salts, water-lean solvents, liquid-liquid solvents, catalysts, polymeric membranes, temperature swing adsorption (TSA), and electro-chemical separation (fuel-cells) have been identified as technologies with potential to advance over the next few years. While most of the post-combustion technologies have some potential to decrease LCOE costs, electro-chemical separation has been identified as the technology with the highest potential to lower the LCOE. It should be noted that this technology (specifically, Molten Carbonate and Solid Oxide Fuel Cells for power plants) has been assessed in more depth within the IEAGHG technical study 2019/03 [2].

Table 2 Overview of development of post-combustion capture and high-temperature solids-looping processes (based on literature review)

TECHNOLOGY		TRL AT PREVIOUS REVIEW	CURRENT TRL	CURRENT DEVELOPMENT TRAJECTORY	PREDICTED LCOE DECREASE C.F. STANDARD TECHNOLOGY
Liquid absorbents	Aqueous amine	6–9	6–9	→	Low
	Amino acid and other mixed salts	–	6	↑	Low
	Ionic liquids	1	4	↓	–
	Encapsulated absorbents	1	2–3	→	–
	Water-lean absorbents	–	5	↑	Medium
	Precipitating	4–5	4–6	→	Medium
	Liquid–liquid separating	4	4–5	↑	Low
	Catalysts	1	6	↑	Medium
Membranes	Polymeric membranes	6	6	↑	Low
	Membrane contactors	–	5–6	→	Medium
	Hybrid processes	6	6	↑	Medium
Solid sorbents	Pressure-swing adsorption (PSA) and temperature-PSA	3	6	→	Medium
	Temperature swing adsorption	1	6	↑	Medium
	Ca looping	6	6	→	Medium
Cooling and liquefaction	3	5	→	Medium	
Electrochemical separation	1	4	↑	High	
Algae-based capture	1	4	↓	–	
Direct air capture	–	5	→	–	

↑ = the technology has commercial backing, and/or large scale evaluation/ demonstration of the technology is either currently underway or planned

→ = while there may be ongoing pilot-scale demonstrations, there are no plans at present for larger-scale demonstration, or the technology is not being progressed by a commercial partner

↓ = while some pilot or laboratory-scale evaluation has occurred, current research is at a less advanced scale than previous levels



Predicted LCOE decrease C.F standard technology: Low: <10%; Medium: 10%-30%; High: >30%, compared to 30w.t.%MEA-based chemical absorption

There is some potential on the development and cost reduction of specific oxyfuel technologies in the case of chemical-looping and pressurised oxyfuel combustion (Table 3).

Table 3 Overview of development of oxyfuel and chemical-looping combustion processes (based on literature review)

TECHNOLOGY	TRL AT PREVIOUS REVIEW	CURRENT TRL	CURRENT DEVELOPMENT TRAJECTORY	PREDICTED LCOE DECREASE C.F. STANDARD TECHNOLOGY
Pressurised oxyfuel combustion	–	5	→	Medium
Oxyfuel gas turbines	2–5	2–5	↑	Low
High-temperature air-separation membranes	4–7	4–7	→	Low
Chemical-looping combustion	2	4–5	→	Medium

Pre-combustion technologies have not increased their TRL significantly since 2014. However, there is room for cost reduction in the sorption-enhanced water-gas shift technology in the near future (Table 4).

Table 4 Overview of development of pre-combustion capture processes (based on literature review)

TECHNOLOGY	TRL AT PREVIOUS REVIEW	CURRENT TRL	CURRENT DEVELOPMENT TRAJECTORY	PREDICTED LCOE DECREASE C.F. STANDARD TECHNOLOGY
H ₂ separation membranes	5	5–6	→	Low
CO ₂ separation membranes	5	5–6	→	Low
Solid sorbents	–	5	→	Low
Chemical liquid absorbents	–	5	→	Low
Sorption-enhanced water–gas shift	5	4–6	→	Medium
Sorption-enhanced reforming	–	4	→	Low
Clathrates	–	4	→	Low



3. Techno-economic assessment of selected CO₂ capture technologies for coal and gas-fired power plants

The results presented in this section are the product of a cost-review assessment. As no modelling work was carried out the accuracy of these results is limited by a number of assumptions:

- The costs reported in the literature were updated by plant size, currency and location.
- The costs were extracted from high-quality assessments found in the available literature. However, there could be technological improvements since these assessments which could result in an increase or a reduction in the costs. Subsequent updates have not been included here.
- There was no bottom-up exhaustive cost evaluation. This means that the contingency costs and the items included in each cost category (CAPEX, OPEX) are based on the information and methodology included in each case extracted from the literature. However, this work set out to provide transparent information and the cost estimations, methodologies and contingency costs are explained in detail.

Three scenarios were considered: the base case scenario, based on the economic and financial parameters used in former IEAGHG studies; and other two scenarios covering sensitivity analyses on the fuel cost, discount rate, plant lifetime, and CO₂ transport and storage costs. The resulting LCOE values were analysed to evaluate the potential of the selected technologies in coal and gas-fired power plants for different financial and economic situations. The results are presented in Figure 1 and Figure 2 and Tables 4 and 5.

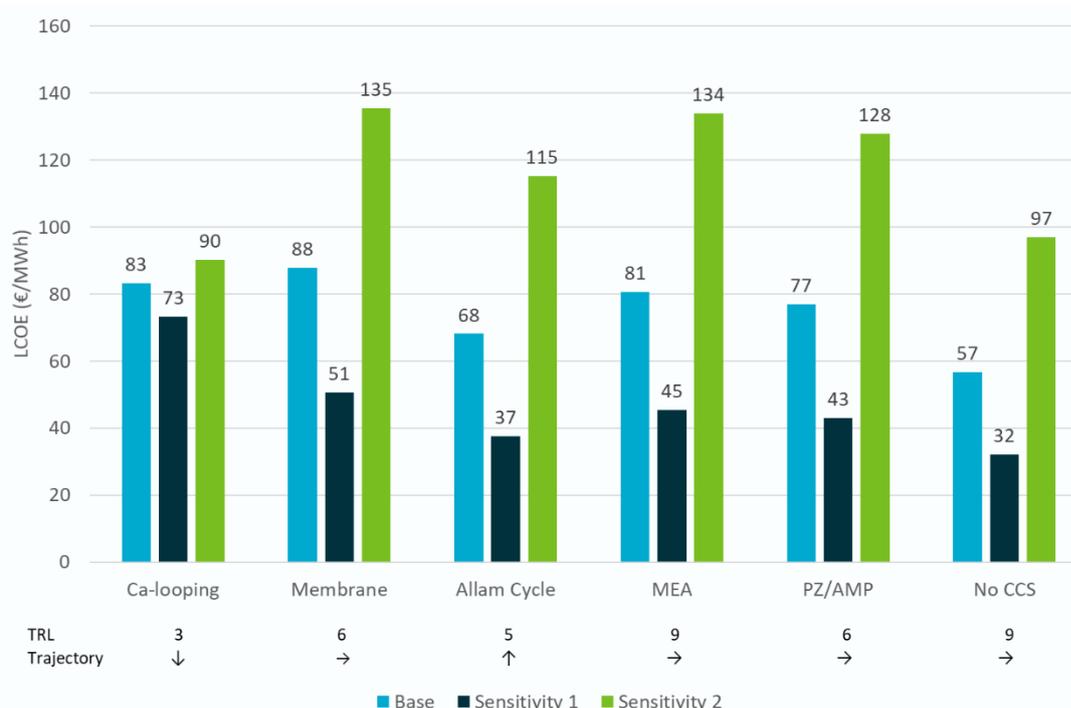




Figure 1 Comparison of levelised cost of electricity (LCOE) of gas-fired technologies
 CCS = carbon capture and storage; MEA = monoethanolamine; PZ/AMP = piperazine/amino-methyl-propanol

Table 5 Criteria used to evaluate the levelised cost of electricity (LCOE) of gas-fired technologies.

SCENARIO	GAS PRICE (€/GJ)	DISCOUNT RATE (%)	PLANT LIFE (YEARS)	CO ₂ TRANSPORT & STORAGE COST (€/TCO ₂)
Scenario 1: Base Case	3	5	40	0
Scenario 2: Sensitivity 1	6	8	25	10
Scenario 3: Sensitivity 2	12	10	25	20

In gas-fired power plants, as seen in Figure 1, the Allam cycle system shows the lowest LCOE under two of the economic scenarios (Scenarios 1 and 2). However, Ca-looping would be the cheapest technology under the Scenario 3 (higher fuels and T&S costs, and higher discount rate), but the most expensive under the second scenario (cheaper fuels and T&S prices, and lower discount rate). It should be mentioned that Ca-looping is at a lower TRL and, consequently, the level of confidence of the related economic assessments needs to be treated with caution.

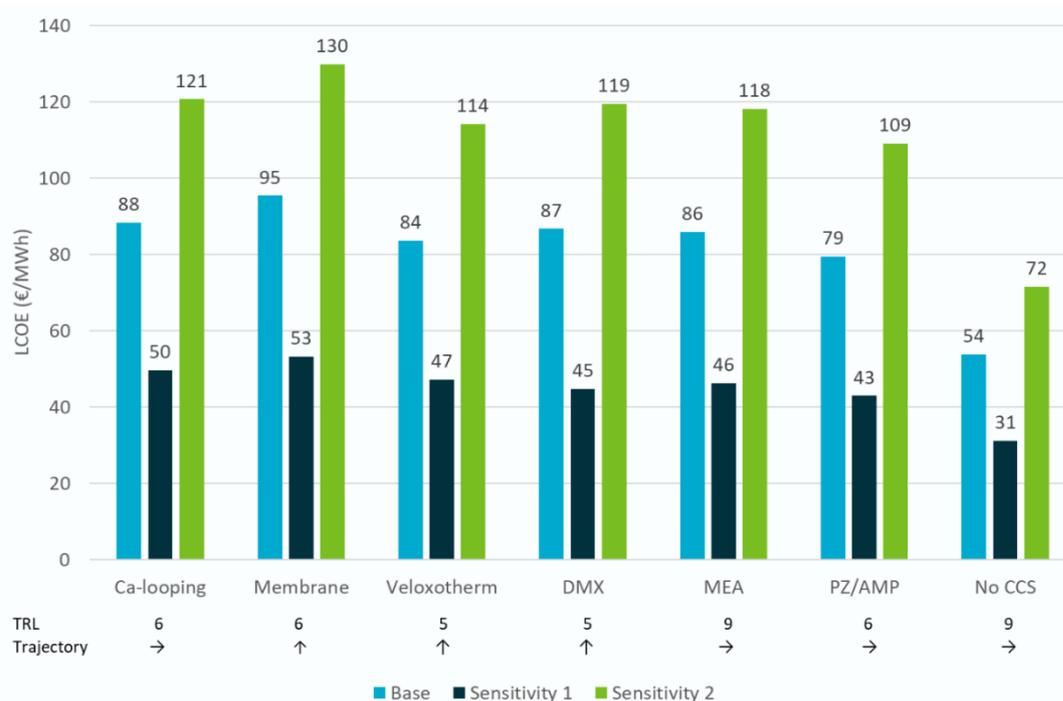


Figure 2 Comparison of levelised cost of electricity (LCOE) of coal-fired technologies
 CCS = carbon capture and storage; DMX = proprietary process developed at French Petroleum Institute Energies Nouvelles; MEA = monoethanolamine; PZ/AMP = piperazine/amino-methyl-propanol.



Table 5 Criteria used to evaluate the levelised cost of electricity (LCOE) of coal-fired technologies.

SCENARIO	COAL PRICE (€/GJ)	DISCOUNT RATE (%)	PLANT LIFE (YEARS)	CO ₂ TRANSPORT & STORAGE COST (€/TCO ₂)
Scenario 1: Base Case	1	5	40	0
Scenario 2: Sensitivity 1	2.5	8	25	10
Scenario 3: Sensitivity 2	4	10	25	20

In coal-fired power plants the impact of the key economic parameters is noticeable which is evident from the differences between the LCOE values for the different scenarios. These differences are higher by comparison with gas-fired power plants (Figure 1). However, the LCOE obtained from the assessment of the different CO₂ capture technologies is more homogeneous than in gas-fired power plants. The new benchmark solution (PZ+AMP) shows the lowest LCOE under all three scenarios, although under the second scenario (cheaper fuels and T&S prices, and lower discount rate), the LCOE values are not significantly different. The membrane-based technology, however, shows a higher LCOE under the three scenarios evaluated.

Based on the results depicted in Figure 1 and Figure 2, it is difficult to decide which technology has the least impact on the LCOE. It is important to consider that the economic review is limited by the location (Netherlands in this study) and plant size. In addition, the cost of each technology has not been assessed uniformly and the systems are at different TRLs. Site and region-specific conditions, based on local circumstances, might also influence the economic framework.

Expert Review Comments

A review was undertaken by four recognised international experts from the industrial sector and academia. The draft was generally well received, with reviewers remarking on the significant contribution of this report to the future CO₂ capture context.

The main comments and suggestions made by the reviewers were related to the status of several technologies, mainly membrane-based and solids-looping systems. In addition, the role of solid looping technologies and their potential in the industrial sector was highlighted, which, although mentioned in this report, is outside its scope.

Although the contractor has reviewed a wide range of well-established and emerging CO₂ capture technologies, few systems at very early stage (TRL 1-4) may not have been included. This study focused exclusively on updating the technologies that were evaluated in the previous IEAGHG 2014 report [1] and providing an overview of systems at TRL 4-9.

In order to show transparent information, the contractor included an analysis of the contingency costs and cost methodologies used in the assessment of each case.



Conclusions

In this study, a new benchmark solution has been proposed: 40w.t.% PZ + AMP (1:2 molar ratio) for chemical absorption, combined with absorber intercooling and rich split flow. This solution represents the current state of the art, assessed in terms of reboiler duty and, reflecting the values reported by commercial technology suppliers. Operating a CO₂ capture system based on this new benchmark would imply a reduction on the CO₂ avoidance cost of 22% and 15% in coal and gas-fired power plants respectively, compared to the 30w.t.% MEA solution.

Chemical absorption is still the leading CO₂ capture technology, although other CO₂ capture systems have advanced since the previous IEAGHG assessment [1]. Their potential to reduce the LCOE was reviewed, and electro-chemical separation (fuel-cells) was identified as one of the potential leaders to cut down costs in the next 5-10 years. In addition, oxyfuel turbines are expected to advance in the near-future, and several systems could offer some LCOE reduction.

The results of the economic assessment presented here, covering Ca-looping, membrane-system (MTR Polaris), Allam Cycle, and chemical absorption (using 30w.t.% MEA and 40w.t.% PZ+AMP) for gas-fired power plants, and Ca-looping, membrane-system (MTR Polaris), Solid sorbent-system (Veloxotherm), liquid-liquid separating system (DMX), and chemical absorption (using 30w.t.% MEA and 40w.t.% PZ+AMP) for coal-fired power plants, should be treated with discretion. It is important to highlight that these results were not assessed with a detailed evaluation based on cost-modelling or a standardised framework. The assessment only shows an overview of the results published in the literature, adapted by plant size, currency, and location (Netherlands).

Recommendations

It is recommended that IEAGHG should continue to maintain a watching brief of emerging CO₂ capture/separation technologies for the power sector as part of the decarbonising technologies portfolio.

It is recommended that future assessments of CO₂ capture technologies should include a comparison with the new benchmark solution. From a technical perspective, the reboiler duty showed by the new benchmark solution was 2.46 and 3.00 GJ/t CO₂ for the USCPSC (Ultra-super critical pulverised coal) and NGCC (natural gas combined cycle) power stations respectively. These values reproduce the performance of enhanced proprietary systems.

From an economical perspective, the analyses presented in this work on the 30w.t.% MEA and 40w.t.% PZ+AMP-based chemical absorption systems were done under a specific economic and financial framework. Future economic studies should either be done under the same criteria or the results here should be adapted to the new techno-economic criteria.



Based on the results, the IEAGHG Project manager suggests the following areas for further work:

- A complete economic analysis on the selected technologies, including detailed modelling, calculations and analysis of inaccuracies under the same economic framework and with details on the contingency cost assessment.
- A follow up on the technologies with the highest potential to reduce the LCOE values. It is recommended to update this report within 5 years to determine the status of the CO₂ capture technologies assessed in this study and evaluate the predictions.
- A complete analysis of the value of the selected technologies, including not only the economics, but their integration in the plant, electricity grid and LCA (Life Cycle Assessment).
- An assessment of advanced and emerging CO₂ capture technologies for the main large emitting intensive industries
- Long-term pilot tests under real conditions. These results will increase the confidence placed on different CO₂ capture technologies and will improve the accuracy of the cost estimates.

References

[1] IEAGHG, *Assessment of emerging CO₂ capture technologies and their potential to reduce costs*, 2014/TR4, December 2014

[2] IEAGHG, *Review of Fuel Cell technologies with CO₂ capture for the power sector*, 2019/03, April 2019

Further assessment of emerging CO₂ capture technologies for the power sector and their potential to reduce cost

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Executive summary

Introduction

Carbon dioxide capture and storage (CCS) is identified as one of the main strategies to reduce CO₂ emissions from the power and industrial sectors. To encourage the early take-up of CCS, much effort in recent years has focused on decreasing the cost and energy penalty associated with CO₂ capture. Although several planned, large-scale demonstration projects have been abandoned globally in the past decade, some first-generation CO₂ capture technologies have been successfully demonstrated and moved on to commercial deployment. However, it is still possible to reduce the cost and improve the efficiencies of these first-generation facilities. There is also significant scope to increase the efficiency of emerging second and third-generation technologies while decreasing their capital and operational costs.

As the development of CO₂ capture technologies continues, new and improved benchmark technologies that are more efficient and cheaper than earlier generations become available. To capitalise on this, the information on new, improved technologies must be disseminated effectively to the general public, policy makers, academia and industry.

The objectives of the current technical study are therefore to:

- a) review carbon-capture technologies and their development status
- b) update the CO₂ capture benchmark technology
- c) draw up a list of promising technologies expected to reach commercial status within the next 10 years
- d) identify the potential risks and barriers for those technologies to reach commercial deployment
- e) provide a list of conclusions and recommended areas for future research.

Part I of this report reviews current and emerging CO₂ capture research, with a focus on technologies applied to the power sector. Projects and technologies that have progressed to pilot-scale demonstration – that is, a technology readiness level (TRL) of 4 to 6 – are summarised, along with information on techno-economic assessments and energy requirements. These technologies are expected to start having an impact and see further demonstration in the next 5–10 years. The section concludes with a discussion on the commercialisation potential of the technology. This evaluates the increase in each technology's TRL since the previous review completed by the International Energy Agency Greenhouse Gas (IEAGHG) Research and Development Programme in 2014, and also considers any potential roadblocks to large-scale deployment of the technology. Part I also contains a more detailed assessment of technologies that have progressed to TRL 4–6. Five of these (membranes, liquid–liquid separating, calcium looping, solid sorbents and oxyfuel gas turbines) are selected for more detailed economic analysis and evaluated for their potential to reduce capture costs into the future.

Part II considers whether a standard liquid-absorption plant using 30 wt% monoethanolamine (MEA) is still the best baseline for comparing emerging technologies. Recent progress in amine-based post-combustion capture (PCC) means that current commercially available technologies will have significantly better performance than the conventional MEA benchmark. This section of

the report explores the technology characteristics that underlie this improved performance, forming the basis for the definition of a new baseline technology. Rather than select the ‘best’ technology among available commercial options, Part II defines an open-source technology that lends itself to independent analysis and comparison.

A more in-depth overview of each part of the report is provided below.

Part I: Review of emerging technologies

Several technologies highlighted in the IEAGHG 2014 review have now progressed to pilot-scale demonstration. In Tables 1–3 below, we provide a snapshot of the development of post, oxyfuel and pre-combustion capture technologies, respectively. The TRL of each technology is compared with the 2014 review, highlighting developments over the past five years (for TRL definition used in this report, see Table 9). Arrows are used to indicate the development trajectory of the technology, as follows:

- An upwards arrow indicates that the technology has commercial backing, and/or that larger-scale evaluation or demonstration of the technology is either currently underway or planned.
- A sideways arrow indicates that while there may be ongoing pilot-scale demonstration of the technology, there are either no current plans for further larger-scale demonstrations, or the technology is not being progressed by a commercial partner.
- A downwards arrow indicates that while some pilot or laboratory-scale evaluation has occurred, current research is at a lower scale than previously.

We also reviewed cost estimates and front-end engineering design (FEED) studies to give insight into potential cost reductions (i.e. reduction in levelised cost of electricity, LCOE) compared with first-generation CO₂ capture technologies (i.e. 30 wt% MEA). The results were summarised into three categories: Low = LCOE decrease <10%; Medium = LCOE decrease 10–30%; High = LCOE decrease >30%.

Table 1 Overview of development of post-combustion capture and high-temperature solids-looping processes

TECHNOLOGY		TRL AT PREVIOUS REVIEW	CURRENT TRL	CURRENT DEVELOPMENT TRAJECTORY	PREDICTED LCOE DECREASE C.F. STANDARD TECHNOLOGY
Liquid absorbents	Aqueous amine	6–9	6–9	→	Low
	Amino acid and other mixed salts	–	6	↑	Low
	Ionic liquids	1	4	↓	–
	Encapsulated absorbents	1	2–3	→	–
	Water-lean absorbents	–	5	↑	Medium
	Precipitating	4–5	4–6	→	Medium
	Liquid–liquid separating	4	4–5	↑	Low
	Catalysts	1	6	↑	Medium
Membranes	Polymeric membranes	6	6	↑	Low
	Membrane contactors	–	5–6	→	Medium
	Hybrid processes	6	6	↑	Medium

TECHNOLOGY		TRL AT PREVIOUS REVIEW	CURRENT TRL	CURRENT DEVELOPMENT TRAJECTORY	PREDICTED LCOE DECREASE C.F. STANDARD TECHNOLOGY
Solid sorbents	Pressure-swing adsorption (PSA) and temperature-PSA	3	6	→	Medium
	Temperature swing adsorption	1	6	↑	Medium
	Ca looping	6	6	→	Medium
Cooling and liquefaction		3	5	→	Medium
Electrochemical separation		1	4	↑	High
Algae-based capture		1	4	↓	–
Direct air capture		–	5	→	–

Table 2 Overview of development of oxyfuel and chemical-looping combustion processes

TECHNOLOGY	TRL AT PREVIOUS REVIEW	CURRENT TRL	CURRENT DEVELOPMENT TRAJECTORY	PREDICTED LCOE DECREASE C.F. STANDARD TECHNOLOGY
Pressurised oxyfuel combustion	–	5	→	Medium
Oxyfuel gas turbines	2–5	2–5	↑	Low
High-temperature air-separation membranes	4–7	4–7	→	Low
Chemical-looping combustion	2	4–5	→	Medium

Table 3 Overview of development of pre-combustion capture processes

TECHNOLOGY	TRL AT PREVIOUS REVIEW	CURRENT TRL	CURRENT DEVELOPMENT TRAJECTORY	PREDICTED LCOE DECREASE C.F. STANDARD TECHNOLOGY
H ₂ separation membranes	5	5–6	→	Low
CO ₂ separation membranes	5	5–6	→	Low
Solid sorbents	–	5	→	Low
Chemical liquid absorbents	–	5	→	Low
Sorption-enhanced water–gas shift	5	4–6	→	Medium
Sorption-enhanced reforming	–	4	→	Low
Clathrates	–	4	→	Low

Our assessment highlights that while important, cost is not the only driver for a particular technology to be considered desirable for further development. Following this assessment, we summarised technologies that had progressed to pilot-scale evaluation and determined their potential for widespread deployment in the next 5–10 years in more detail. To assist with this, a set of metrics was established to indicate the technologies’ attractiveness for further development based on:

- level of demonstration achieved
- potential for cost reduction
- use and experience in industries other than CCS
- availability of components

- ease of retrofit
- further engineering or research and development required for CCS.

A ranking was applied to each assessment category, which allowed an overall score to be calculated for each technology. These are summarised in Table 4.

Table 4 Summary of rankings attributed to technologies based on their potential for widespread deployment in the next 5-10 years

SCORE	POST COMBUSTION CAPTURE TECHNOLOGIES	OXYFUEL PROCESSES	PRE-COMBUSTION CAPTURE TECHNOLOGIES
19	Amine based liquid absorbents		
18	Electrochemical separation		
17	Solid sorbents (PSA, VPSA, TPSA); calcium looping		H ₂ separation membranes; CO ₂ separation membranes; solid sorbents
16	Liquid-liquid separating, non-aqueous and non-amine; amino acid and other mixed salt; solid sorbent (TSA)		Chemical liquid absorbents
15	Catalysts and other activators	Chemical looping combustion	
14	Precipitating processes; membranes; membrane contactors; cooling processes		Sorbent enhanced water gas shift
13		Oxyfuel gas turbines; high temperature air separation membranes	
12	Ionic liquids	Pressurised solid oxyfuel combustion	
11			Clathrates

Finally, we selected five representative technologies for a more detailed analysis of their potential to reduce the cost of CCS in coal and natural-gas-fired power plants. This selection was based on the technology ranking, its current level of development, and wider interest as evidenced by plans for ongoing larger scale demonstration or further research funding. In the second half of this report, an updated benchmark technology is proposed to reflect the current state-of-the-art performances anticipated for liquid absorption-based CO₂ capture. We then compared the five selected technologies with the former standard for PCC (30 wt% MEA), and the updated standard, a piperazine/amino-methyl-propanol (PZ/AMP) blend (see Part II of this report). The purpose of this assessment was not to provide accurate costs for the different technologies considered, because final project costs will be significantly influenced by site-specific conditions. Rather, our aim was to use information in the public domain to provide an indication of the cost range that new and emerging CO₂ capture technologies are anticipated to achieve. As the information is taken from cost studies available in the literature, there will be different assumptions between the studies that will affect the final cost data. This will affect the capital and operating cost information used when calculating a levelized cost of electricity (LCOE). Ideally one would adapt the bare erected cost data from the different literature studies for the same assumptions. Unfortunately, some of the studies provided insufficient detail to allow back-calculation of the bare erected equipment cost. Instead we have used scaling factors to adapt the cost studies to the same plant location (The Netherlands), and scaled the technologies to the same unit size. Where possible we have also averaged costs over a range of different studies. Tables 5 and 6 provide an overview of the literature used in the LCOE

calculations, including the different cost methodologies followed, for natural gas and coal-fired technologies, respectively. Further detail is provided in Appendix A.

Two sensitivity cases as determined by the range of fuel cost, discount rate, plant life and CO₂ transport and storage costs were also evaluated, and LCOE values were scaled to the PZ/AMP unit size (i.e. 761 MW_{net} for the gas-fired plant and 684 MW_{net} for coal). Costs for natural-gas combined-cycle (NGCC) plants are provided in Figure 1, and coal-based plants in Figure 2.

Table 5 Summarised information of cost studies used in calculation of LCOE for natural gas-fired technologies

TECHNOLOGY	REFERENCE	COST METHODOLOGY FOLLOWED	ORIGINAL PLANT LOCATION	PROJECT, PROCESS CONTINGENCY
No CCS	This study	IEAGHG	Greenfield site, The Netherlands	10% of Total installed cost 16% of Total installed cost applied to CCS
MEA	This study	IEAGHG	Greenfield site, The Netherlands	10% of Total installed cost 16% of Total installed cost applied to CCS
AMP/PZ	This study	IEAGHG	Greenfield site, The Netherlands	10% of Total installed cost 16% of Total installed cost applied to CCS
Allam cycle	IEAGHG 2015	IEAGHG	Greenfield site, The Netherlands	10% of Total installed cost Process contingency not applied
	White and Weiland 2018	NETL 2011	Greenfield site, Mid-west USA	15% of Total installed cost 20% of Total installed cost (5% on instrumentation and control)
Ca Looping (with exhaust gas recycle)	Hu and Ahn 2017	NETL 2013 followed for reference NGCC plant.	Information not provided	Information not provided
Membrane (with exhaust gas recycle)	van der Spek et al. 2018	European benchmarking task force for NGCC design. Cost based on methodology of Rubin et al. 2013	Rotterdam, The Netherlands	40% Total installed costs (project contingency)

Table 6 Summarised information of cost studies used in calculation of LCOE for coal-fired technologies

TECHNOLOGY	REFERENCE	COST METHODOLOGY FOLLOWED	ORIGINAL PLANT LOCATION	PROJECT, PROCESS CONTINGENCY
No CCS	This study	IEAGHG	Greenfield site, The Netherlands	10% of Total installed cost 16% of Total installed cost applied to CCS
MEA	This study	IEAGHG	Greenfield site, The Netherlands	10% of Total installed cost 16% of Total installed cost applied to CCS
AMP/PZ	This study	IEAGHG	Greenfield site, The Netherlands	10% of Total installed cost 16% of Total installed cost applied to CCS
Ca Looping	Mantripragada and Rubin 2014		Retrofit, USA	22% of direct capital cost 21% of direct capital cost
	Hanak and Manovic 2017			Information not provided
	Rolfe et al. 2017, 2018	EU best practice guidelines	Retrofit	10% Total capital investment (project contingency)
	Abanades et al. 2015			Information not provided
DMX	Broutin et al. 2017	EU best practice guidelines	Europe	Information not provided
VeloxoTherm	NRG Energy 2016	NETL 2013	Greenfield site, Mid-west USA	15-30% of Total plant cost 20% of Total plant cost (applied to novel technology)
Membrane	Merkel et al. 2016	NETL 2013	Greenfield site, Mid-west USA	15-30% of Total plant cost 20% of Total plant cost (applied to novel technology)
	NETL 2012	NETL 2010	Greenfield site, Mid-west USA	15-30% of Total plant cost 20% of Total plant cost (applied to membrane, 15% applied to CPU)

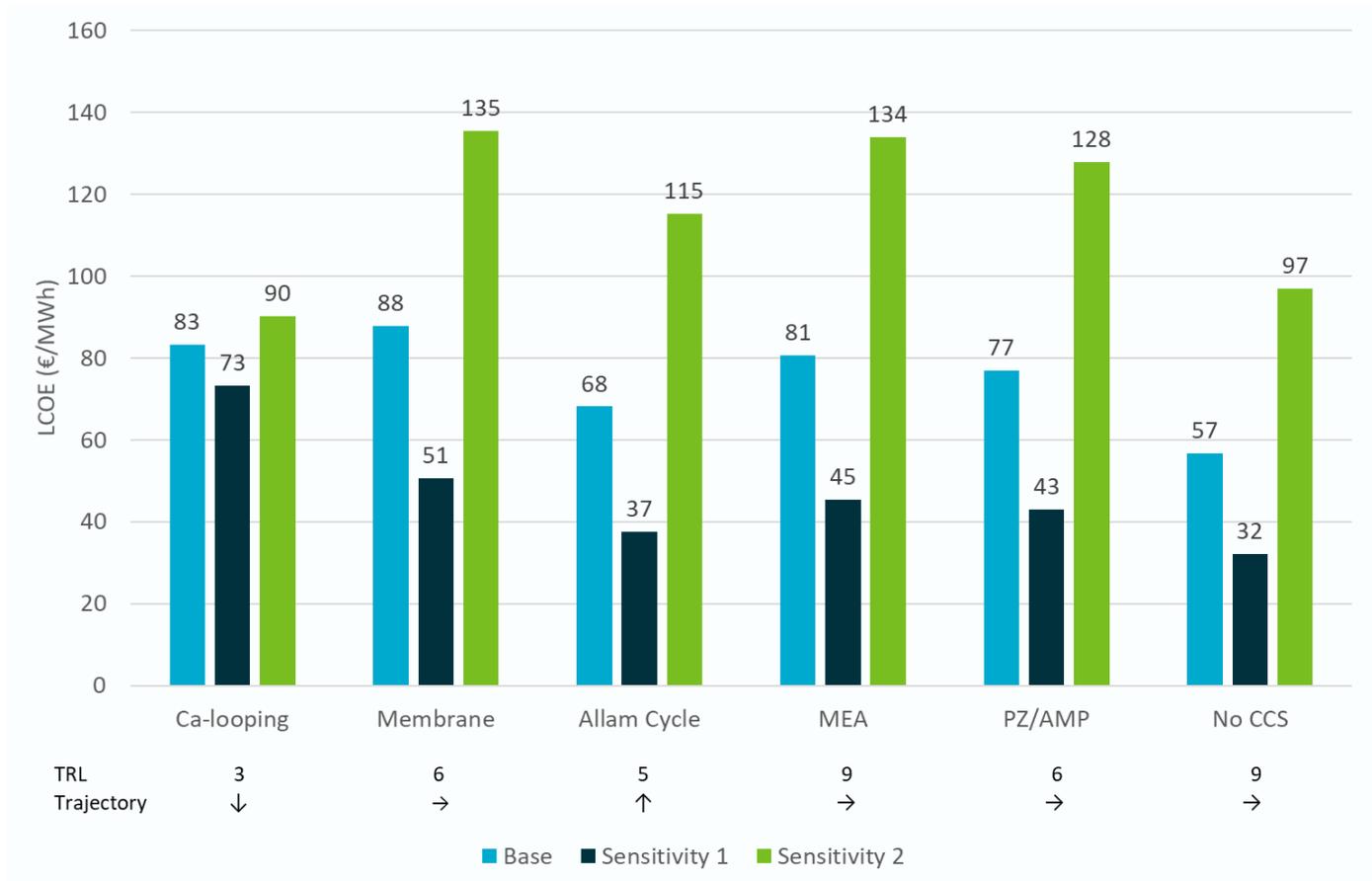


Figure 1 Comparison of levelised cost of electricity (LCOE) of gas-fired technologies

CCS = carbon capture and storage; MEA = monoethanolamine; PZ/AMP = piperazine/amino-methyl-propanol
 Values used for sensitivity analysis, with base case results in bold. Gas price 3/6/12 €/GJ, Discount rate 5/8/10 %, Plant life 40/25/25 years, CO₂ transport and storage cost 0/10/20 €/tCO₂

Changes to fuel cost, discount rate, plant life and CO₂ transport and storage costs have a significant impact on the LCOE, but this is fairly uniform across technologies. Under the base scenario, the CO₂-capture cost and CO₂-avoidance costs are below ~100 €/tCO₂ for gas-fired and below ~60 €/tCO₂ for coal-fired technologies. These costs are within the range of future carbon-price trajectories. Therefore, with a carbon price in place, these technologies would be cost effective.

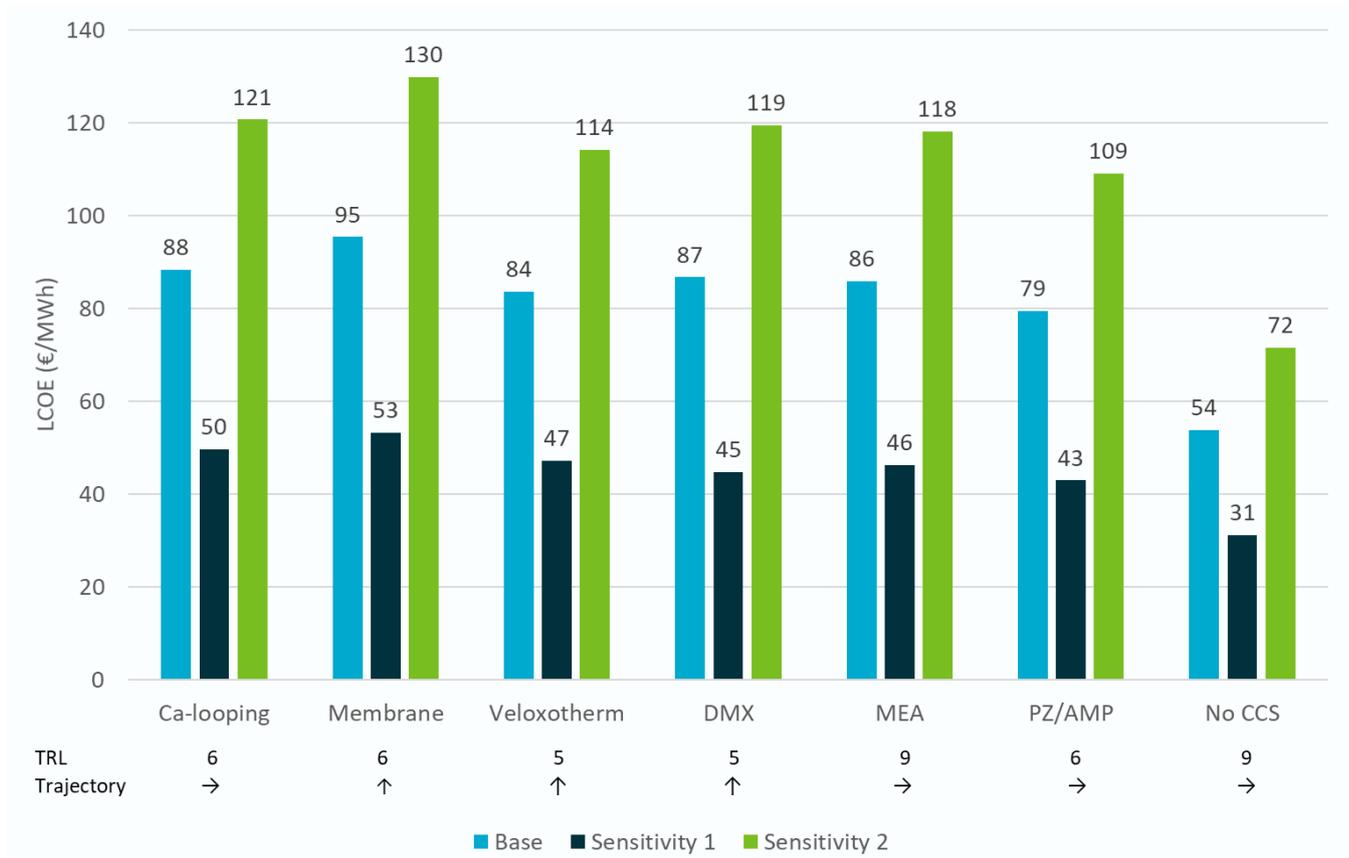


Figure 2 Comparison of levelised cost of electricity (LCOE) of coal-fired technologies

CCS = carbon capture and storage; DMX = proprietary process developed at French Petroleum Institute Energies Nouvelles; MEA = monoethanolamine; PZ/AMP = piperazine/amino-methyl-propanol
 Values used for sensitivity analysis, with base case results in bold. Coal price 1/2.5/4 €/GJ, Discount rate 5/8/10 %, Plant life 40/25/25 years, CO₂ transport and storage cost 0/10/20 €/tCO₂

We then used CSIRO’s Global and Local Learning Model–Electricity (GALLM-E) to project the future cost of electricity-generation technologies. GALLM-E is a global and local endogenous experience curve model for projecting future uptake and cost of electricity generation technologies. We updated the model to include the new ‘baseline’ technology, PZ/AMP. These results are highlighted in Figure 3. By 2030, the LCOE for PZ/AMP is projected to decrease by 15% for coal-fired and 6% for gas-fired power plants.

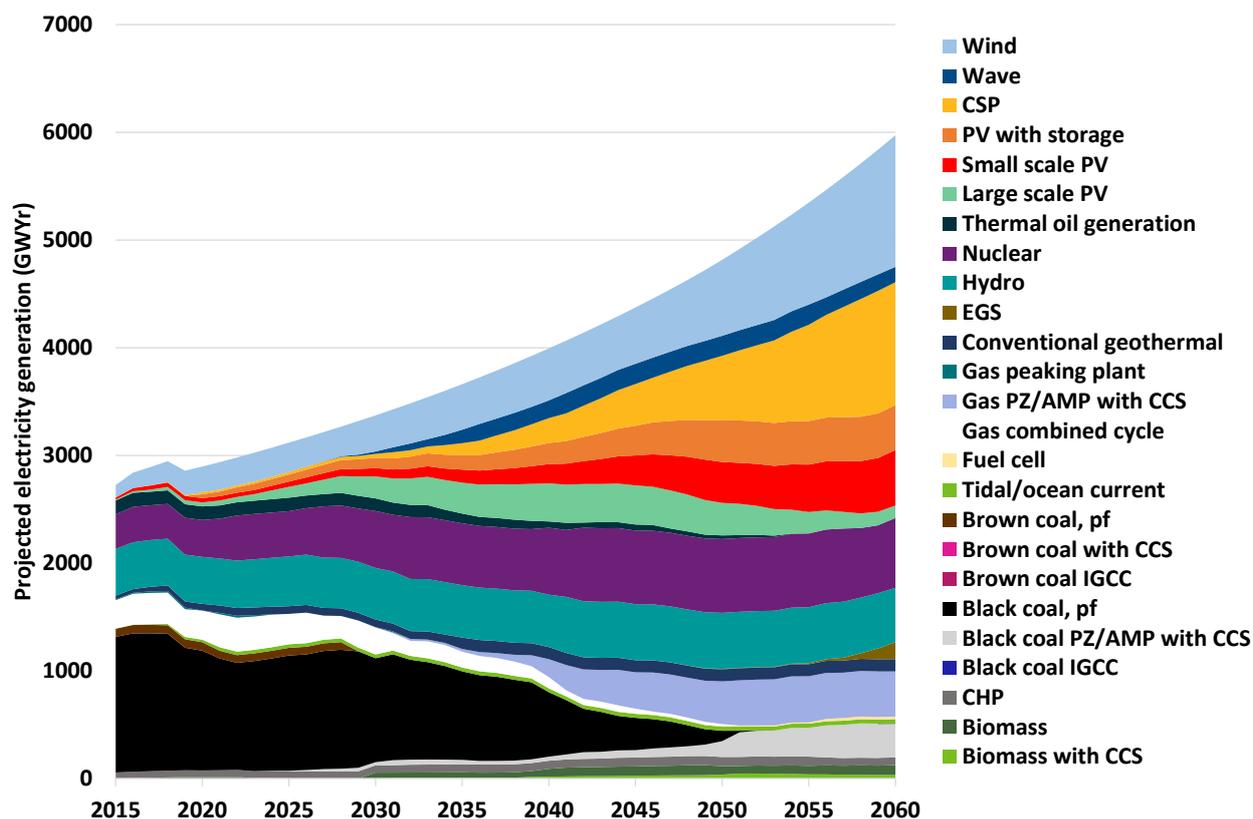


Figure 3 Projected electricity generation under a two-degree carbon-price scenario

CCS = carbon capture and storage; CHP = combined heat and power; CSP = concentrating solar power; EGS = enhanced geothermal system; IGCC = integrated gasification combined-cycle; pf = pulverised fuel; PV = photovoltaic; PZ-AMP = piperazine/amino-methyl-propanol

In the final section of Part I, we assess barriers to widespread deployment of the technologies. For most technologies, FEED studies have made use of currently available components. Where components are not available, collaboration with industry and technology suppliers has been used to de-risk processes as much as possible. The results highlight that although the technological barriers to widespread deployment are being addressed, of greater hindrance are elements that will likely be experienced for most large-scale CCS projects: high commercial risk and investment cost, particularly when enhanced-oil-recovery options are not available for revenue from CO₂ sales. In addition to the need for legislation around CO₂ storage, additional challenges for CCS projects include uncertain political and public support.

Part II: Updating the benchmark technology

For many years, 30 wt% MEA has been used as the benchmark PCC technology against which new and improved technologies are compared. Amine-based liquid absorbent CO₂ capture technology has seen significant development in the last 5–10 years. Current, commercially available technologies have shown better techno-economic performances than the baseline MEA process.

Thus, it is essential to update the benchmark technology to ensure that any potential benefit arising from future technology developments are visible against current commercial offerings. The new benchmark should reflect the performance of current state-of-the-art PCC technologies. To this end,

we assessed the technical performance characteristics of commercially available amine technologies as available in the public domain. An overview of these properties is provided in Table 7. It is important to note that commercial technology developers were not approached to assist with this assessment. We recognise that the most up-to-date information on commercial technologies is often not shared publicly. However, for the purpose of this review – identifying the performance targets for the proposed new benchmark – the information available in the public domain was deemed to be sufficient.

Table 7 Comparative overview of amine-based, post-combustion CO₂-capture technologies

TECHNOLOGY SUPPLIER	REBOILER DUTY GJ/tCO ₂	ABSORPTION LIQUID FLOW m ³ /tCO ₂	ELECTRICITY CONSUMPTION kWh/tCO ₂	AMINE/AMMONIA IN EXHAUST ppm	AMINE CONSUMPTION kg/tCO ₂
Mitsubishi Heavy Industries	2.6 (coal)	10 (coal)	77 (coal)	Amine: 0.7–3 Ammonia: 0.3–2.0	0.35
Shell Cansolv	2.2–2.8 (coal) 2.3–2.9 (gas)	10–16	70 (coal) 100 (gas)	Not found	0.1
Fluor	3.2 (coal) 3.6 (gas)	17	38–40 (coal) 53–125 (gas)	Amine: 0.1–1.0 Ammonia: 1.3–2.2	1.6
Aker Solutions	2.8 (9% CO ₂) 3.4 (gas)	11.4–14.2	Not found	Amine: 0.02 Ammonia: 0.1	0.2–0.6
BASF-Linde	2.7 (coal)	Not found	22	Amine: 0.3–0.5	0.3
Toshiba	2.4–2.6 (coal)	17	Not found	Not found	Not found
Hitachi	2.4 (coal)	Not found	Not found	Not found	Not found

We hypothesised that the current process performances, as reported by the technology suppliers, could be reproduced through amine process modelling with suitable formulations. For this purpose, we modelled an ultra-supercritical coal-fired power station and a natural-gas combined-cycle in EBSILON® in accordance with the IEAGHG technical and economical assessment criteria. This generated the flue-gas streams for which PCC options with alternative amine formulations were explored. While a large number of formulations are possible, the analysis focused on those amines for which ample information was available in the public domain, and for which process modelling could be carried out using standard gas-treatment software.

In this study, ProTreat® was used to simulate the CO₂-capture process. We selected a 40 wt% formulation of PZ/AMP in a 1:2 molar ratio as representative of the current state of the art and used a CO₂-capture rate of 90%. A PCC process configuration with absorber intercooling and rich-split flow was selected to reflect the fact that technology suppliers use a variety of process designs to optimise performance. The specific reboiler duties determined reflected those reported by the suite of technology suppliers. Finally, we carried out a techno-economic evaluation of the PCC process. This indicated that the costs of capture with respect to 30% MEA for the coal-fired power station were reduced by 22% and for the NGCC by 15%. The results of our evaluation are summarised in Table 8.

Table 8 Overview of techno-economic assessment for two types of power plants without (W/O) post-combustion capture (PCC), with capture via 30 wt% MEA, and with capture using a PZ/AMP blend

	Ultra-supercritical coal-fired power plant			Natural-gas combined-cycle power plant		
	W/O PCC	MEA	PZ/AMP	W/O PCC	MEA	PZ/AMP
Technical performance						
Gross power output (MW)	900	900	900	890	890	890
Auxiliary power (MW)	83	266.1	215.6	12	161.8	128.2
Net power output (MW)	817	633.9	684.4	878	728.2	761.9
Net plant higher heating value efficiency (%)	42.5	32.97	35.59	52.66	43.91	45.94
Net plant lower heating value efficiency (%)	44.4	34.48	37.23	58.25	48.57	50.82
CO ₂ generation (t/h)	604	604	603.3	310	310	310
CO ₂ emission (t/h)	604	61	59.1	310	31	31
CO ₂ emission (t/MWh)	0.739	0.095	0.084	0.353	0.042	0.040
CO ₂ capture (t/h)	0	543	544	0	279	279
Equivalent energy consumption (MWh/tCO ₂)	–	0.337	0.244	–	0.506	0.423
Economic performance						
Total capital requirement (million €)	1342.8	1681.1	1659.5	835.7	1172.8	1166.3
Specific capital requirement (€/kW)	1647	2654	2424	939	1611	1531
Fixed operations & maintenance (O&M) (million €)	37.7	46.3	45.9	29.2	39.7	39.5
Variable O&M (million €)	7.54	20.1	17.8	3.41	11.9	9.1
LCOE (€/MWh)	51.6	87.0	79.5	52.9	77.6	73.8
CO ₂ avoided cost (€/tCO ₂)	–	55.0	42.8	–	79.3	67.1

Note: CO₂ emissions include CO₂ contained in the combustion air. The LCOE values in Table 8 follow those calculated in IEAGHG 2019-02, and use different fuel and T&S costs compared to those calculated in Part I of this report.

Recommendations

This report suggests the following recommendations:

- Long-term, pilot-scale evaluation treating real process flue-gas streams is required to build confidence in any new technology. Information gathered from these demonstrations should be used to update techno-economic analyses.
- It is important that demonstrations progress for a range of technologies. This is to ensure a portfolio of technology demonstrations so that the program is robust to a single failure. In addition, choice of technology options will increase competition and cost reduction.
- The costs of different technologies must be compared over a consistent baseline. Wider sharing of FEED studies and cost estimates will also build confidence in results.

- The current baseline for comparing new technologies must be updated. Almost all technologies now see a cost benefit compared with the previous standard (30 wt% MEA). The new baseline proposed here, a generic and publicly available PZ/AMP blend, has anticipated costs comparable to those estimated for emerging CO₂ capture technologies.

Part I Review of capture technologies, costs and barriers to deployment

1 Introduction

The International Energy Agency Greenhouse Gas (IEAGHG) Research and Development Programme explored promising capture technologies and their potential to reduce costs in its Technical Review, *Assessment of emerging CO₂ capture technologies and their potential to reduce costs* (IEAGHG 2014). This document included a review of post-combustion, pre-combustion and oxyfuel combustion capture technologies, and systems with circulating solids.

Several important conclusions were drawn from the IEAGHG study. For example, reductions in cost and energy consumption for new capture technologies, or those at earlier stages of development, were found to be over-optimistic. Similarly, while promising reductions were implied for technologies in which CO₂ capture played a more integral part of the power-generation process, e.g. in solids-looping combustion and certain types of fuel cell, those too were considered insufficiently advanced to bring the required confidence to stakeholders, funders and investors.

The range of technologies, both existing and emerging, applicable to CO₂ capture from pre, post and oxyfuel combustion conditions has been reviewed previously (IEAGHG 2014, Lockwood 2016, Bui et al. 2018). The purpose of this report is to review new and emerging technologies for CO₂ capture, with a focus on those with the potential for widespread deployment in the near term. This review will have a particular focus on the likely cost of emerging technologies, and consideration of potential roadblocks to future, large-scale development.

The vast majority of research work and economic assessments completed to date have focused on the application of CO₂ capture to the power industry, and are the focus of this report. More recently focus has shifted to the application of CCS technologies to other industries, particularly in Europe. Some information on CO₂ capture projects applied to industry are included in the sections reviewed here. For more detail on industrial applications of CCS, readers are directed to the relevant IEAGHG technical reviews, for example, *Cost of CO₂ capture in the industrial sector: Cement and iron and steel Industries* (IEAGHG 2018), *Understanding the cost of retrofitting CO₂ capture in an integrated oil refinery* (IEAGHG 2017), and *Deployment of CCS in the cement industry* (IEAGHG 2013).

The initial selection of a particular CO₂ capture technology requires a comprehensive understanding of the technology status and its potential for cost reduction. The technology status is usually described by its technology readiness level (TRL). As such, an estimation of the TRL is provided for the technologies considered. Comparison is made to the 2014 IEAGHG review, which provides an indication of the progress achieved in the last five years. The previous review used the definition for TRL as provided by the Electric Power Research Institute (EPRI). As such, the same definition will be followed here for consistency, and is outlined in Table 9.

Technology readiness does not necessarily relate directly to potential for large-scale commercialisation. A high TRL is certainly important and necessary, as it provides an understanding of the level of in-service evaluation and demonstration the technology has achieved. It does not, however, provide information on other potential roadblocks to commercialisation, such as ability for mass production, or availability of supporting technologies (e.g. compressors), particularly at a large scale.

Table 9 Description of technology readiness levels (IEAGHG 2014)

	TECHNOLOGY READINESS LEVEL	DESCRIPTION
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 relevant environment
	5	Sub-system validation in relevant environment
	4	System validation in laboratory experiment
Research	3	Proof-of-concept tests, component level
	2	Formulation of the application
	1	Basic principles observed, initial concept

The following four sections provide an overview of a range of technologies currently being evaluated for capture of CO₂. These include post-combustion capture (PCC) technologies (Section 2), high-temperature solids-looping processes (Section 3), oxyfuel combustion technologies (Section 4), and pre-combustion capture technologies (Section 5). For each type of technology, we consider the level of demonstration achieved, and assess the potential for widespread deployment in the future.

Following these overviews, Section 6 covers the technologies anticipated to see impact within the next 5–10 years, and investigates their potential to reduce costs. Section 7 contains our conclusions and recommendations for future PCC research and development.

2 Post-combustion capture technologies

Post combustion CO₂ capture processes involve removing the CO₂ from a gas stream after the combustion process, as outlined in Figure 4. This section covers seven main types of PCC technologies:

- liquid absorbents
- membranes
- adsorbents
- cooling and liquefaction
- electrochemical separation
- microbial and microalgae
- direct air capture.

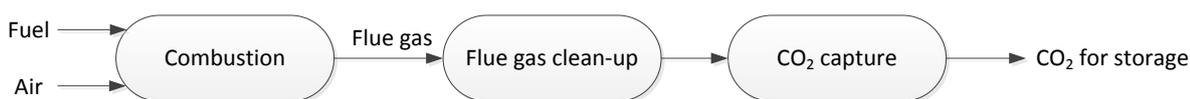


Figure 4 Post combustion CO₂ capture process

2.1 Liquid absorbents

Liquid absorbents fall into eight categories, each of which is discussed separately below. These include advanced amines, phase-separating absorbents, ionic liquids, non-amine and non-aqueous (water-lean) absorbents, microencapsulation, amino acid and other mixed-salt absorbents, catalysts and other activators, and combined capture concepts.

2.1.1 Advanced amines

For PCC applications, the most technologically advanced process is absorption of CO₂ into solutions of aqueous amines and amine blends. The standard process is a cyclic absorption/desorption process, as outlined in Figure 5. There are several technologies already offered commercially, having been demonstrated successfully in other industries. Application to large-scale CO₂ capture from coal-fired power plants, however, is still limited, with only two commercial facilities in operation to date. Their widespread use in other industries, such as natural-gas processing, leads to them have a high TRL. There are still development challenges, as the volumetric gas flows to be treated are significantly larger and flue-gas conditions are oxidative in nature.

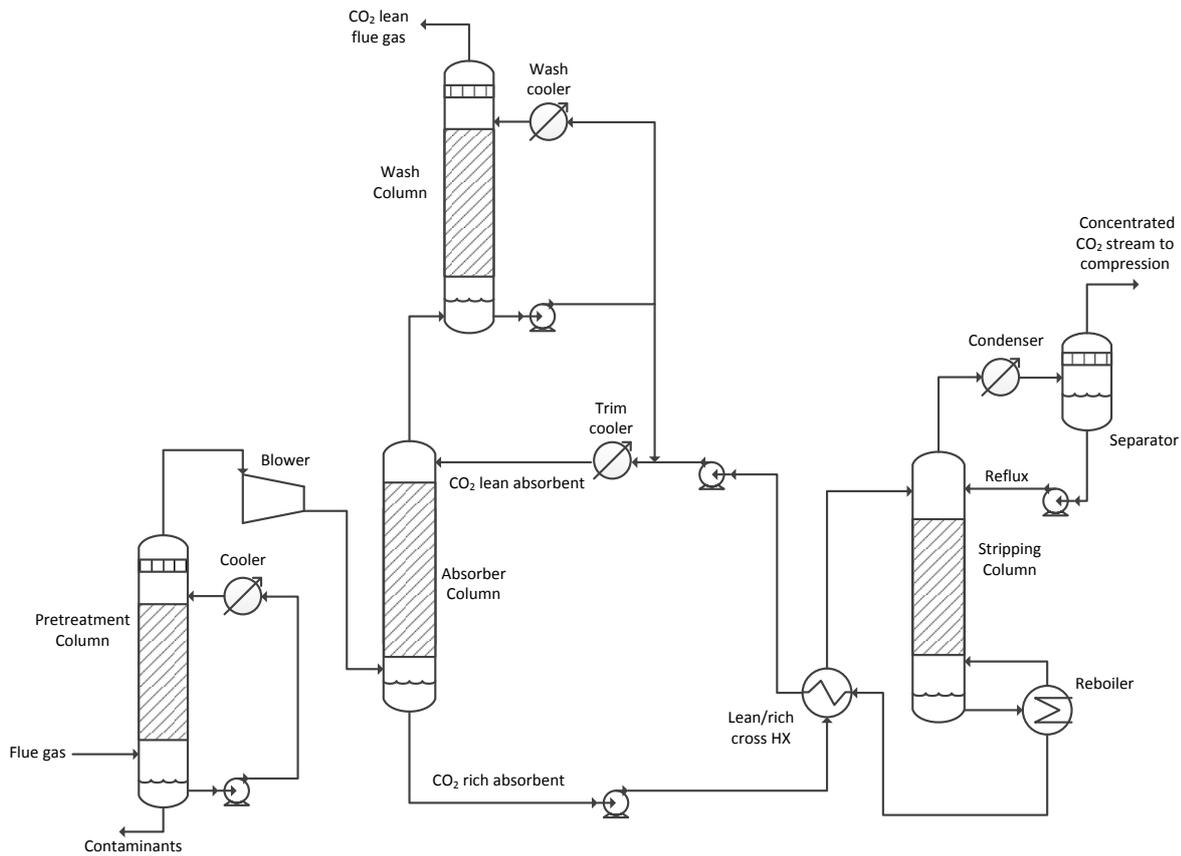


Figure 5 Liquid absorption-based CO₂ capture process

In the previous IEAGHG report (2014), the benchmark monoethanolamine (MEA) absorbent was viewed as being at a TRL of 9, with newer absorbents achieving TRLs in the range of 6–8. With the establishment of two commercial facilities located at coal-fired power plants, the Shell Cansolv process at Saskpower’s Boundary Dam power plant and Mitsubishi Heavy Industries (MHI) KM-CDR process at the NRG-owned WA Parish Power Station, these technologies can now also claim to be at commercial level. In addition to these, several other commercial vendors offer similar CO₂-capture technologies based on aqueous amines. Further detail on these processes are available in Part II of this report.

Significant research and development work has been undertaken to improve on the currently available commercial offerings, with a large number of amine absorbents analysed for their ability to capture CO₂ (Singh and Versteeg 2008, Puxty et al. 2008). In addition to mass-transfer rates and energy requirements, amine degradation and emission rates are also important. It is essential that amine properties and characteristics are not considered in isolation, and that their effect on the overall process is taken into account.

Mota-Martinez et al. (2017) completed a screening assessment in which the thermo-physical aspects of potential absorbents were analysed for their overall effect on the cost and environmental aspects of PCC. Their results suggest that while equilibrium CO₂ capacity is a key determinant of process performance, transport properties (e.g. viscosity) and other thermo-physical properties (e.g. heat capacity) also have a significant effect on the capital cost, and thus on the cost of the captured CO₂. When evaluating a new absorbent for PCC, properties that have a primary importance for the total annual cost of CO₂ capture are: viscosity > equilibrium loading of CO₂ > reaction kinetics >> heat capacity > heat of absorption > density > surface tension (Mota-Martinez et al. 2017).

Another important factor is the cost, or anticipated cost, of the new absorbent. An evaluation by Hitachi and the University of Kentucky showed that while next-generation absorbents had much lower consumption than MEA, the higher amine cost mitigated much of the cost advantage due to lower make-up requirements (Nikolic 2017). It is important to note however that the overall capital cost of the system can have a far greater impact on the levelised cost of electricity than solvent make-up costs.

Raksajati et al. (2018) used Monte Carlo simulation to investigate the effect of absorbent properties on overall system cost. They found that good stability towards SO_x and NO_x, low heat of reaction (<50 kJ/molCO₂), high absorption rate, low water-vaporisation rate and low absorbent cost were the most critical parameters influencing cost. They suggest that an absorbent with these properties comparable to those achievable today, then capture costs of \$53–55/tCO₂ avoided (USD 2011) should be possible for systems including flue-gas pre-treatment.

While significant research is under way developing the next generation of improved absorbents for PCC, only a few have made it through to pilot-scale evaluation on real flue gases. This is a critical step in determining real online efficiencies, energy requirements, absorbent degradation rates and emissions. All of this information is critical for completing economic evaluations with greater accuracy. Table 10 summarises amine absorbents that have progressed to pilot-scale evaluation on real industrial gas streams (i.e. a TRL of 6 or above).

Table 10 Overview of aqueous amine and amine-blend absorbents that have been evaluated at pilot scale

TECHNOLOGY, COMPANY/RESEARCH INSTITUTE	DESCRIPTION	COST AND ENERGY INFORMATION	REFERENCES
ISOL-162 IHI	Technology combines new amine blend, new process and advanced packing 20 t/d evaluation in Japan 5000 h evaluation at Loy Yang pilot plant, Australia, treating coal combustion flue gas	40% lower energy than conventional 30 wt% MEA 2.4–2.6 GJ/tCO ₂	Okuno et al. 2017 Nakamura et al. 2014
CASTOR CESAR	Absorbents developed as part of CASTOR and CESAR projects Evaluated at Esbjerg pilot plant treating coal combustion flue gas CASTOR absorbent loss comparable to MEA (~1.4 kg amine/tCO ₂) despite lower degradation rates	CASTOR absorbents achieved steam consumption 3.6 GJ/tCO ₂ CESAR absorbents achieved steam consumption 2.9–3.1 GJ/tCO ₂	Knudsen et al. 2009 Knudsen et al. 2011
OASE® Blue BASF-Linde	Evaluated at Niederaussem (0.45 MW _e) and National Carbon Capture Center (NCCC) (1.5 MW _e) pilot plants Absorbent consumption 0.3 kg/tCO ₂ (achieved at Niederaussem pilot plant) Stripper operating pressure 3.4 bar _a Installation of upstream bag filter lowered emissions and absorbent loss at NCCC Received recent Department of Energy (DOE) funding for 15-MW _e pilot plant to be constructed at University of Illinois Abbott power station	Evaluation at NCCC achieved specific reboiler duty (SRD) 2.7 GJ/tCO ₂ Techno-economic assessment compared with DOE/ National Energy Technology Laboratory (NETL) case 12 Power plant efficiency increased from 28.4 to 31.4% (with advanced process) Cost of electricity 125.5 \$/MWh (c.f. 147.2 \$/MWh for MEA process), and CO ₂ -capture cost of 39.90 \$/MTCO ₂ (c.f. 56.49 \$/MTCO ₂ for MEA process)	Stoffregen et al. 2014 Moser et al. 2013 Jones and Krishnamurthy 2017

TECHNOLOGY, COMPANY/RESEARCH INSTITUTE	DESCRIPTION	COST AND ENERGY INFORMATION	REFERENCES
Advanced carbon capture (ACC) process Aker Solutions	Achieved 50,000 operating hours in 6 pilot plants globally Developed and operated mobile test unit evaluating performance on various process gas streams 2-year evaluation completed at Technology Centre Mongstad (TCM) (evaluating absorbents S21 and S26). 0.2–0.3 kg amine/tCO ₂ absorbent loss for S26 (c.f. 2.6 kg amine/tCO ₂ for MEA) 18 months evaluation of ACC (absorbent S26) at cement plant in Brevik	SRD of 3.4 GJ/tCO ₂ achieved at TCM treating combined heat and power (CHP) flue gas (standard layout), 10% lower than 30 wt% MEA. SRD of 2.8 GJ/tCO ₂ achieved for absorbent S26 when treating flue gas with 9% CO ₂ and using Energy Saver concept Heat integration between desorber and CO ₂ compression plant expected to reduce reboiler steam demand to ~2 GJ/tCO ₂ Evaluation at cement plant achieved 2.8–3.2 GJ/tCO ₂ (standard plant layout)	Knudsen 2017 Knudsen et al. 2017 Knudsen et al. 2014 Gorset et al. 2014
CAL008 CSIRO	5,000 h evaluation completed at 'PICA' (Post-combustion carbon capture, IHI, CSIRO, AGL) pilot plant in Australia treating coal combustion flue gas	2.9 GJ/tCO ₂ using standard configuration 2.6 GJ/tCO ₂ achieved using process modifications	Webster-Gardiner et al. 2018
Concentrated piperazine (PZ) University of Texas	Pilot-scale evaluation on synthetic flue gas of 5 m and 8 m PZ CO ₂ removal rates up to 97% achieved. Foaming controlled with anti-foam agent. Regeneration via advanced flash stripper 1700 h operation achieved with 8 m PZ at Tarong pilot plant, Australia, using standard configuration 2,000 h evaluation completed at NCCC (0.5 MW _e); 90–98% CO ₂ capture achieved, NH ₃ emissions below 5.5 ppmV	2.1–2.5 GJ/tCO ₂ with advanced flash stripper 2.1 GJ/tCO ₂ achieved at NCCC with advanced flash stripper producing CO ₂ at 6 bar	Rochelle et al. 2018 Chen et al. 2017 Cousins et al. 2015
APBS PCCmax CDRMax Carbon Clean Solutions	Evaluation at Netherlands Organisation for Applied Scientific Research (TNO) pilot plant at EON power station (1000 h); 10 times more stable than MEA (based on NH ₃ emissions) Evaluation of CDRMax at NCCC (pilot solvent test unit, simulated natural-gas flue-gas results reported) and TCM Absorbent emissions below 1 ppmV and NH ₃ below 2 ppmV for duration of 3-month campaign at TCM (~1200 h)	2.8 GJ/tCO ₂ with standard flow sheet (2.6 GJ/tCO ₂ anticipated with process modifications) 3.1 GJ/tCO ₂ achieved on simulated natural-gas flue gas at NCCC 2.8 GJ/tCO ₂ estimated with optimised lean/rich cross HX (90% capture) 3.25 GJ/tCO ₂ achieved at TCM	Bumb et al. 2014 Bumb et al. 2017
Research Institute of Innovation Technology for the Earth (RITE, Japan)	Developed advanced amine absorbents for CO ₂ removal from iron and steel industry Evaluated at 1 t/d and 30 tCO ₂ /d pilot plants treating blast furnace gas Absorbent regeneration at T <100 °C Ongoing research & development focusing on development of new amines targeting 20 \$/tCO ₂	2 GJ/tCO ₂ achieved in 2012	Chowdhury et al. 2017 Onoda et al. 2016
H3-1 Mitsubishi Hitachi Power Systems	Evaluated at 0.7-MW _e pilot scale at the University of Kentucky Center for Applied Energy Research pilot plant with secondary air stripper Thermal stripper pressure 5.2 bar	2.62 GJ/tCO ₂ (based on simulations)	Heberle et al. 2017 Thompson et al. 2018

TECHNOLOGY, COMPANY/RESEARCH INSTITUTE	DESCRIPTION	COST AND ENERGY INFORMATION	REFERENCES
	Ongoing work evaluating process modifications at pilot-scale including pre-concentrating membrane and water wash	Initial economic evaluation using DOE/NETL case 10 suggests 46.9 \$/tCO ₂ -capture cost (c.f. 61.3 \$/tCO ₂ for MEA process), and LCOE 164.3 \$/MWh (c.f. 189.6 \$/MWh for MEA process)	
Advanced liquid-absorption system ION Engineering	Water-lean absorbent incorporating amine blend 1000 h evaluation at NCCC (PTSU, 0.6 MW _e) Evaluation also completed at TCM (12 MW _e)	2.5 GJ/tCO ₂ expected 3.6 GJ/tCO ₂ achieved at NCCC; however, system was not optimised for absorbent, and achieved capture efficiencies >95% (NGCC) 3.4 GJ/tCO ₂ achieved at TCM (4.1% CO ₂ , 90% capture) When CO ₂ increased to 12.5 vol% and stripper pressure increased, 3.3 GJ/tCO ₂ achieved Independent economic assessment showed 38% reduction in incremental capital cost and 28% reduction in operating and maintenance cost compared with standard MEA process Total cost of CO ₂ capture 39–45 \$/tCO ₂	Brown et al. 2017 Meuleman et al. 2017 ION Engineering 2018
Chilled Ammonia Process (CAP) GE (formerly Alstom)	22,000 h operation in pilot and validation facilities on range of flue-gas streams, with capture efficiencies up to 96% achieved Pilot operations showed benefit of precipitation was marginal, hence ongoing operation in non-solids mode 75–90% capture achieved on American Electric Power (AEP) Mountaineer pilot (20 MW _e). Build-up of ammonium bisulphate resulted in additional stripper being installed 6000 h operation at TCM; 85–87% capture achieved, NH ₃ emissions 2–4 ppmV This process is now being evaluated for application to the cement industry as part of the CEMCAP project	Economic evaluation after Mountaineer trials determined efficiency penalty of 9.5% and LCOE increase of \$59/MWh 1.9 GJ/tCO ₂ estimated based on theory 2.6 GJ/tCO ₂ achieved at pilot scale (with solids precipitation) 3.9 GJ/tCO ₂ achieved at pilot scale operating in non-solids mode (89% capture) 3.0 GJ/tCO ₂ achieved at TCM treating natural-gas flue gas (87% capture) 2.6 GJ/tCO ₂ (85% capture) achieved treating residue fluid catalytic cracker flue gas When applied to cement plant, economic evaluation suggests specific primary energy consumption for CO ₂ avoided of 3.75 GJ/tCO ₂ and cost of 66 €/tCO ₂ avoided	Augustsson et al. 2017 CEMCAP 2018 Voldsund et al. 2018
RS-2 Doosan Babcock	Completed 2-year pilot-plant campaign at Ferrybridge power station (5 MW _e)		Fitzgerald et al. 2014

Lowering the cost of liquid-absorbent-based PCC via improving the standard process flow sheet has also been explored. Most of the efforts have been adapted from those suggested in natural-gas processing plants. These concepts can be readily applied to most liquid-absorbent-based

PCC; however, the effectiveness of each modification will depend of the specifics of the CO₂-capture absorbent. The ability of these modifications to reduce cost was explored in IEAGHG 2014/08. Several of these modifications have been evaluated at pilot scale and are incorporated into commercial plant design. More recent developments include the secondary air stripper as evaluated by the University of Kentucky (Heberle et al. 2017). Absorbents able to withstand higher regeneration pressures and temperatures could see benefit using the advanced flash stripper concept being developed by the University of Texas (Rochelle 2018). Technologies focused on reducing the capital cost of CO₂-capture plants include the rotating liquid sheet contactor (Wardhaugh et al. 2015) and rotating packed bed (Lee et al. 2017) concepts.

Discussion on commercialisation potential and development since previous review

Liquid amine absorbents are generally considered to be at a high TRL for PCC, having already received significant use in other industries. The potential scale of system required for PCC is certainly much larger than used previously, with sizing of columns and blowers a potential concern. Steps have been made in this area with two commercial-scale plants now currently operating. However, CO₂ capture from the full flue-gas volume of a 500–800-MW unit will still likely require multiple trains. Large-scale columns are likely to have different designs, e.g. tile-lined square concrete columns in use at Technology Centre Mongstad (TCM) and Boundary Dam. Manufacturing methods will need to improve to avoid potential leakage issues.

GE has noted that for their chilled ammonia process, limitations for scale-up include: practical limit on the absorber vessel diameter, and a limitation on the available chiller size. There are also potential limitations on the size of high-pressure slurry pumps (for precipitating process) and heat exchangers. Based on this information, it was determined that the largest size train for a commercial unit would be limited to 200–400 MW for a single train.

For advanced amine absorbents, the large-scale manufacture and synthesis of novel amines is a potential roadblock. For some absorbents such as ammonia and piperazine, which already have significant use in other industries, scale-up of manufacturing should be possible. For more novel amines, the establishment of manufacturing at the scale necessary is still required. This will also likely impart an additional cost to novel amine systems in the short term.

The previous review considered liquid-absorbent technology as being at a high level of readiness (TRL 7–9). Since then, additional technologies are now at commercial scale, with a large number also achieving TRLs of 6 or above (further information is provided in Part II of this report). The establishment of two commercially operating plants, and the significant use of the technology in other industries (though at smaller scale), suggests there is no significant technological barrier to the scale-up of liquid-absorbent-based processes for PCC.

2.1.2 Phase-separating absorbents

Precipitating absorbents

An absorbent that precipitates upon absorption of CO₂ can potentially lead to higher recoveries, as it will remove the CO₂ from solution, driving the reaction towards further capture. In addition, the solid phase can be separated, reducing the volume of absorbent requiring regeneration. Designing a system that can provide adequate contact between the gas and absorbent phase, and also deal

with the slurry formed, is challenging. Precipitating absorbents that have been investigated include carbonates (e.g. K_2CO_3 , $(NH_4)_2CO_3$), tertiary amines, amino acids and ammonia. These systems react with CO_2 to form a bicarbonate product or amino acid that precipitates under certain conditions of temperature, concentration, and sometimes pH (Lockwood 2016). As yet, no precipitating processes are operating at an industrial scale for CO_2 capture, as the design and operation of suitable equipment for precipitating systems requires further development (Mumford et al. 2017).

The GE (formerly Alstom) Chilled Ammonia Process (CAP) is one of the more developed precipitating processes for CO_2 capture, as outlined in Table 10. This process has now been evaluated at pilot scale, treating coal combustion flue gas. However, the benefit of the precipitating process was determined to be marginal due to the additional chilling requirements and operational challenges. Hence, ongoing development is focusing on their non-precipitating process (Augustsson et al. 2017).

SINTEF has evaluated precipitating amino acids for CO_2 capture (Aronu et al. 2014), identifying absorbents with cyclic capacities 61% higher than achieved with 30 wt% MEA. Selected absorbents have now undergone initial pilot-scale evaluation (Aronu et al. 2017). An ongoing CLIMIT (Norwegian CCS research programme) project, INSPIRE, aims at further evaluation of this process in collaboration with Westec Environmental Solutions using their novel froth contactor. This contactor was previously evaluated for the precipitating potassium carbonate process (BCIA 2015).

Waseda University and IHI Corporation have evaluated a precipitating amino-methyl-propanol (AMP) system (50 wt%) at bench scale. Absorber temperatures needed to be maintained above $60\text{ }^\circ\text{C}$ to avoid solids precipitation in the column. A regeneration-energy requirement of 2.8 GJ/tCO_2 was estimated via equilibrium-based calculation, and was validated in laboratory-scale experiments. Precipitating AMP blends have also been evaluated by the Lund University (Sanku and Svensson 2017).

Zhejiang University have evaluated blends of piperazine (PZ) with N,N-dimethylformamide at bench scale, forming PZ-carbamate precipitates. The regeneration-energy requirement of the precipitate is estimated at 2.8 GJ/tCO_2 (Li et al. 2018).

The formation of CO_2 -hydrates was evaluated for CO_2 capture as part of the iCap project. The storage capacity of the hydrates, however, was determined to be low. As a consequence, bulk reactor volume and flow rates were high if the process was operated at pressures close to atmospheric. Operation nearer 40 bar was required to lower capital and operating costs. This process was ultimately considered unviable for PCC (NTNU 2015).

A slightly different approach was considered by the University of Notre Dame, who evaluated phase-change ionic liquids for CO_2 capture. These ionic liquids are solid at normal flue-gas-processing temperatures, but form a liquid on reaction with CO_2 (Seo et al. 2014).

Information on additional precipitating CO_2 capture processes that have progressed from laboratory-scale experiments, or for which economic assessments have been completed, is summarised in Table 11.

Table 11 Overview of precipitating absorbents for post-combustion CO₂ capture

TECHNOLOGY COMPANY/RESEARCH INSTITUTE	DESCRIPTION	COST AND ENERGY INFORMATION	REFERENCES
UNO MK3 UNO Technology	<p>Precipitating potassium carbonate process developed through CO₂CRC. Able to remove SO_x and NO_x from flue gas, forming K₂SO₄ and KNO₃ salts. Removing need for pre-treatment lowers system cost. Promoted system designed for 90% capture.</p> <p>Evaluated on laboratory and pilot-scale plant. Pilot-scale facility treating coal flue-gas. Promoted system (glycine) achieved CO₂ capture efficiencies 10–50% with foaming controlled through addition of anti-foaming agent.</p>	<p>2–2.5 MJ/kgCO₂ (simulation)</p> <p>45 \$/tCO₂ avoided (simulation)</p>	<p>Andersen et al. 2013</p> <p>Mumford et al. 2012</p> <p>Smith et al. 2014</p> <p>Smith et al. 2015</p> <p>Smith et al. 2017</p>
Hot-CAP University of Illinois	<p>Hot carbonate absorption process with crystallisation enabled high-pressure stripping. Uses carbonate salt to absorb CO₂ and SO₂ at 70 °C. Rich solution is crystallised to separate bicarbonate slurry. Regeneration at high pressure to lower CO₂ compression work. Evaluated on laboratory-scale absorber/desorber.</p>	<p>Heat duty achieved via experimentation (including heat of crystallisation) 1.8 GJ/tCO₂</p> <p>Preliminary techno-economic assessment completed (DOE/NETL case 10)</p> <p>Net plant efficiency 29% higher heating value (c.f. 26.2% with MEA)</p> <p>LCOE 120.3 \$/MWh (c.f. 75.3 no capture, 139 \$/MWh with MEA)</p>	<p>Lu 2014</p>
Amine-promoted precipitating potassium carbonate Shell	<p>Evaluated on 25 kg/d bench-scale apparatus. Rich solution cooled to initiate precipitation. Crystalliser designed by Delft University of Technology.</p>	<p>2.2–2.5 MJ/kgCO₂ (based on simulation)</p>	<p>Moene et al. 2013</p>
Controlled solids formation – Chilled ammonia process (CSF-CAP) ETH Zurich	<p>Controls solids formation in a dedicated process section, allowing absorber and desorber to be kept solids free.</p> <p>Rich solution is cooled to induce solids formation in crystallisation unit. Solids separated in downstream hydrocyclone.</p>	<p>Aspen simulation suggests specific primary energy consumption for CO₂ avoided of 2.6 MJ/kgCO₂ (standard chilled ammonia process 2.9 MJ/kgCO₂)</p>	<p>Sutter et al. 2017</p>
Amino-silicones GE University of Pittsburgh	<p>Early work screening amino-silicones for CO₂ capture identified some that formed free-flowing solid on reaction with CO₂ (solid carbonate species). The GAP-O amino-silicone has twice the capacity of the liquid-absorbent method.</p> <p>Evaluated in laboratory spray absorber followed by cyclone separation. Stability allows regeneration at high temperatures and pressures. Issue transporting solid phase from low-pressure absorber to higher-pressure regenerator. Screw conveyors identified as most practical method. Second atmospheric polishing desorber added to achieve full absorbent regeneration. Full system evaluated at laboratory scale.</p>	<p>Simulation completed in Aspen suggests first-year CO₂ removal cost of \$52/tCO₂ (c.f. \$66/tCO₂ for MEA). Phase-change process</p> <p>2% more efficient, and 22% lower capital cost than equivalent MEA process.</p>	<p>Perry et al. 2012</p> <p>O'Brien et al. 2014</p> <p>Perry 2016</p> <p>Perry et al. 2017</p>

TECHNOLOGY COMPANY/RESEARCH INSTITUTE	DESCRIPTION	COST AND ENERGY INFORMATION	REFERENCES
DECAB DECAB+ Amino acids– aqueous solutions of potassium taurate and potassium alanate. TNO, University of Delft, Siemens	<p>The DECAB process uses an equimolar mixture of KOH and taurine. Lean solvent used in packed column. Semi-lean absorbent contacted with flue gas in spray column.</p> <p>Under the DECAB+ process, a solid–liquid separator is added downstream of the absorber. K⁺ rich supernatant is recycled to absorber, CO₂ and taurine-rich slurry sent to stripper where lower pH enhances release of CO₂.</p>	<p>DECAB 3.2 GJ/tCO₂ (simulation). 2.8 GJ/tCO₂ estimated using flue-gas heat to re-dissolve crystals.</p> <p>Techno-economic analysis suggests DECAB CO₂ capture costs comparable to MEA system.</p> <p>DECAB+ 2.4 GJ/tCO₂ (35% below MEA baseline 3.7 GJ/tCO₂) based on simulation. 0.96 GJ/tCO₂ also required to re-dissolve crystals – heat to be supplied from low-grade sources.</p> <p>Simulation results suggest reboiler duties as low as 2.1 GJ/tCO₂ achievable when incorporating process modifications (lean vapour recompression) (MEA equiv. 3.2 GJ/tCO₂).</p>	<p>Sanchez-Fernandez et al. 2011</p> <p>Sanchez-Fernandez et al. 2013</p> <p>Sanchez-Fernandez et al. 2014</p> <p>van der Ham et al. 2016</p>
CarbonOrO process	<p>Uses an amine solution to capture CO₂ in a standard absorption/desorption process. Thermoresponsive co-polymer with amine monomer distributed through polymer. Increasing temperature causes phase separation, allowing regeneration at temperatures as low as 70 °C, saving 10–25% in energy compared with conventional processes (regeneration nearer 120 °C). Low-temperature regeneration potentially allows the use of waste heat for regeneration. Current application in biogas upgrading, evaluated at pilot scale in the Netherlands.</p>	<p>Low-temperature regeneration expected to roughly halve capture costs.</p>	<p>CarbonOrO 2018</p> <p>CarbonOrO report summary 2017</p> <p>Custers et al. 2014</p>

Liquid–liquid separating absorbents

Some absorption liquids will separate into two liquid phases based on temperature or absorption of CO₂. This can allow separation of the CO₂-rich phase, minimising the amount of absorbent sent for thermal regeneration, reducing energy requirements and equipment size. An example of a liquid–liquid separating process, the DMX process, is provided in Figure 6. Where the phase separation is caused by the absorption of CO₂, it often derives from the selection of lipophilic amines, which have limited miscibility with the aqueous phase and form two phases under standard conditions (Lockwood 2016). One drawback of these processes is that the CO₂-rich phase is usually much more viscous than the lean phase, resulting in reduced heat transfer and higher pumping costs (Lockwood 2016). Reduced mass transfer resulting from the higher viscosity can also be an issue in the absorption column. Temperature-based separation, where the liquid separates into two phases above a certain temperature, has received some experimental investigation. However, challenges relating to low absorption capacities or volatility (where phase separation occurs at regeneration temperatures) have limited their development (Wang and Xu 2016). To date, most progress in this area has focused on phase separation induced via the absorption of CO₂.

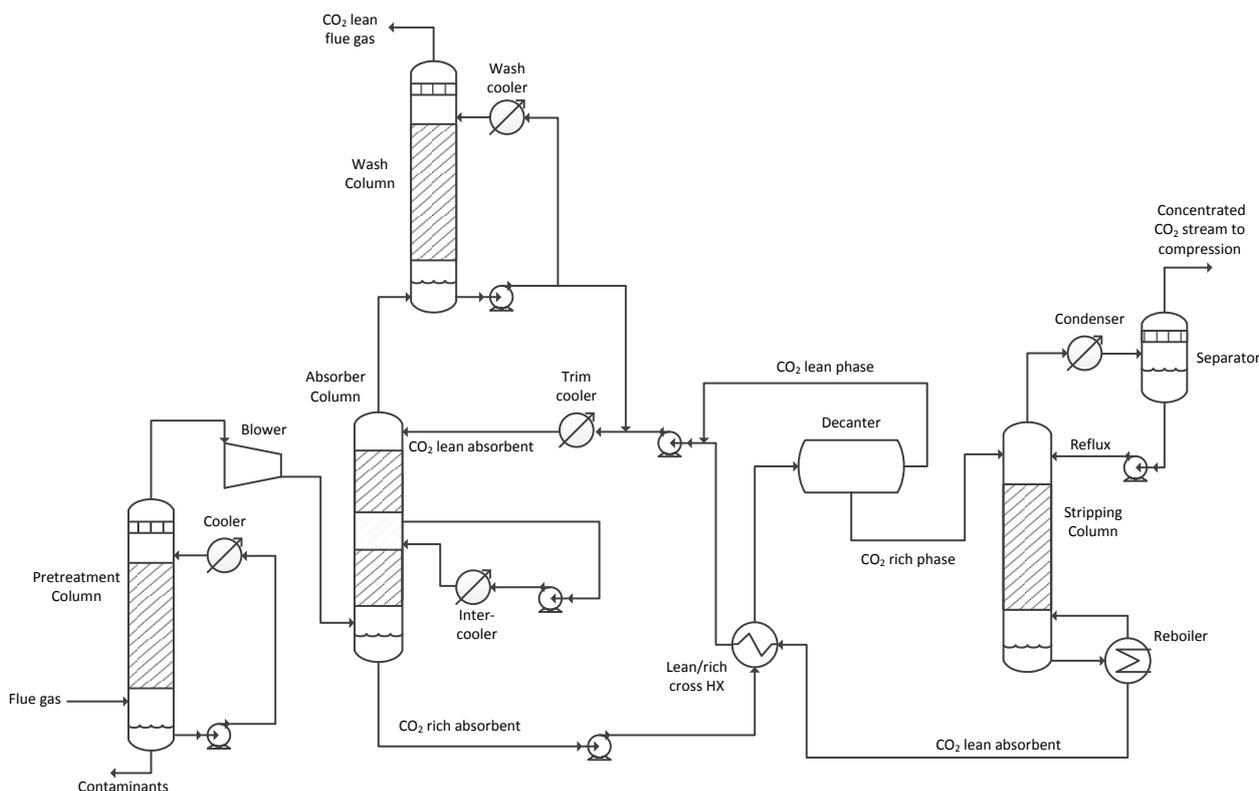


Figure 6 Flow diagram of the DMX process (Broutin et al. 2017)

3H Company's 'self-concentrating absorbent' consists of an amine in a non-aqueous solvent that phase separates on absorption of CO₂. Regeneration energy is estimated to be one-third of 30 wt% MEA (Hu 2012). Yale University are evaluating a concept where an organic solvent is used to extract the CO₂ from a CO₂-rich ammonia solution. This organic solvent is then regenerated using low-temperature heating (Novek et al. 2016). Tsinghua University has completed laboratory screening of mixed amine solutions including 1,4-butanediamine/N,N-diethylethanolamine. Desorption heat for this blend estimated to be 32% lower than 30 wt% MEA, and sensible heat 41% lower (Wang and Xu 2016). The Korean Institute of Energy Research has completed laboratory screening of amine blends as biphasic sorbents (You et al. 2017). They have evaluated phase-separating amine-alcohol blends (Kim et al. 2014), as have Beijing University of Chemical Technology (Zhang et al. 2017) and CanmetENERGY, Canada (Zhuang and Clements 2018), with phase separation for the CO₂-rich sorbent noted to form spontaneously. Water-lean blends of 2-(methylamino)ethanol or 2-(ethylamino)ethanol with bis(2-ethoxyethyl)ether have been evaluated in bench-scale, packed columns by the Institute of Chemistry and Organometallic Compounds, with CO₂ capture efficiencies up to 97.6% achieved (Barzagli et al. 2017). Table 12 provides an overview of additional research and development that has been completed for liquid-liquid phase-separating sorbents for PCC of CO₂.

Table 12 Overview of liquid-liquid phase-separating absorbents for post-combustion CO₂ capture

TECHNOLOGY COMPANY/RESEARCH INSTITUTE	DESCRIPTION	COST AND ENERGY INFORMATION	REFERENCES
DMX (based on 1,3-dipropyl-methyl-xanthine)	Evaluation completed at bench-scale. Planned pilot-scale evaluation at power plant abandoned due to lack of funds.	2.1–2.5 GJ/tCO ₂ (simulation) Capture cost 63 \$/tCO ₂	Raynal et al. 2011 Raynal et al. 2014 Lockwood 2016 Broutin et al. 2017

TECHNOLOGY COMPANY/RESEARCH INSTITUTE	DESCRIPTION	COST AND ENERGY INFORMATION	REFERENCES
French Petroleum Institute Energies Nouvelles (IFPEN), licensed by Axens	More recently IFPEN have evaluated the DMX absorbent for CO ₂ removal from blast furnace gas as part of the VALORCO project. 1500h of operation achieved on mini-pilot at IFPEN operating on synthetic blast furnace gas. High CO ₂ /CO selectivity and high CO ₂ capture rate (99.9%) achieved. DMX absorbent has low corrosivity, allowing the use of lower-cost materials for construction. Chemical and thermal stability also reported to be good allowing higher temperature regeneration, producing CO ₂ at pressures up to 6 bar _a . Pilot-scale operation ongoing.	LCOE 48% increase over conventional 620-MW plant (c.f. 60% increase for MEA process) As part of the OCTAVIUS project, DMX economics benchmarked against 30 wt% MEA. When applied to an 805-MW _e coal-fired power station, DMX process resulted in 2 percentage point lower efficiency reduction. Cost of CO ₂ avoided 42.6 €/tCO ₂ (c.f. 56.5 €/tCO ₂ for 30 wt% MEA). Interestingly, regeneration of DMX at higher pressure (6 bar _a) was found to have a higher efficiency penalty than regeneration at 1.85 bar _a pressure due to the higher pressure steam extraction required for regeneration. Predicted CO ₂ cost of capture 50 \$/tCO ₂ (steam price 25 \$/t) as part of VALORCO project	Dreillard et al. 2017
Blend of a tertiary amine 2-(diethylamino)ethanol (DEEA) and the diamine 3-(methylamino)propylamine (MAPA) SINTEF, Norwegian University of Science and Technology (NTNU)	Initial development under the iCap project. Some concentrations of DEEA/MAPA blends have been found to phase separate. Progressing work on blend of 5 M DEEA, 2 M MAPA. Upon cooling the mixture forms CO ₂ -rich and lean phases. No viscosity or foaming issues noted at pilot-scale operation (synthetic flue gas); however, absorbent was more volatile than MEA. Best energy numbers achieved without circulation of light phase	2.5 MJ/kgCO ₂ by experiment 2.4–3.0 GJ/tCO ₂ achieved at pilot plant	Pinto et al. 2014 NTNU 2015 Knudsen 2017
Aqueous blend of lipophilic secondary and tertiary amines (dipropylamine/ N,N-dimethylcyclohexylamine, N-methylcyclohexylamine), with AMP as solubiliser University of Dortmund	Phase separates upon heating. Regeneration possible at temperatures below 80 °C, CO ₂ capacity 75%>MEA. Foaming and volatility potential issues. Viscosity higher than standard MEA	SRD of 2 MJ/kgCO ₂ estimated based on thermodynamic calculations	Zhang 2013
Biphasic CO ₂ absorption process (BiCAP) University of Illinois at Urbana-Champaign	Screened over 80 formulations. Phase transition tuneable with solvent formulation. Selected absorbent more stable to thermal and oxidative degradation compared with MEA. Multiple intercooling stages on absorber to remove more viscous CO ₂ -rich phase as it generates. Regeneration at elevated pressure evaluated in laboratory-scale flash and stripping column.	Aspen simulation to provide preliminary techno-economic analysis. Cost of electricity (COE) 83 \$/MWh (c.f. 107 \$/MWh for MEA, DOE case 12), cost of CO ₂ captured \$28/tonne (c.f. \$49/tonne for MEA) Currently evaluating at 10-kW _e lab-scale unit to provide information for more detailed cost estimate. Regeneration energy in range 2–2.8 GJ/tCO ₂ depending on regeneration pressure	Lu 2017 Ye et al. 2017 Lu 2018

Discussion on commercialisation potential and development since previous review

While there has been some pilot-scale demonstration of absorbents with potential for phase separation, many have not yet incorporated or demonstrated operation with precipitation and on-stream separation of precipitates. Precipitating processes rely on the phase change only occurring where designed. Precipitation occurring at other stages can be problematic (e.g. blocking pipework or packing material in absorber). During pilot-scale evaluation, systems blockages were noted to be an issue when operating with promoted K_2CO_3 . At this stage, the challenges associated with dealing with the precipitates and slurry formed have not yet been overcome. As a result, many of the organisations developing these systems are currently moving forward with non-precipitating versions of the technology. GE has achieved pilot-scale operation with their precipitating NH_3 process. However, the additional cooling required meant that only minimal benefit was achieved through the precipitating process. As a result, GE is continuing with the development of their non-precipitating NH_3 process. For the GE GAP-0 process, while the screw conveyor worked in the laboratory, the efficiency of heat transfer did not scale favourably. For a 500-MW power station, an extruder would be in the order of 900 mm in diameter. The largest twin-screw conveyor currently on the market is 420 mm in diameter. Thus, alternate conveyance mechanisms and absorbent regeneration are being considered.

In the previous review, precipitating processes were deemed to have reached a TRL of 4–5 based on some pilot-scale evaluation. However, the extent to which solids handling had been demonstrated in a fully integrated system was not fully clear. The move of many companies towards non-precipitating alternatives of their absorbents is perhaps telling. Ongoing research in this area still appears to be predominantly in the early laboratory and experimental phase for precipitating absorbents. Since the previous review, large-scale pilot evaluation of the CO2CRC K_2CO_3 process has been demonstrated treating coal flue gas, but challenges still persist and 90% capture was not achieved. The GE CAP has achieved significant pilot-scale evaluation; however, further progress will be focusing on the non-precipitating process. The GE precipitating amino-silicone process has now been evaluated as a fully integrated process at laboratory scale, but issues with potential scale-up have been identified. The Shell precipitating process does not appear to have received any significant development since the last review. The DECAB process has progressed to DECAB+, with simulations now suggesting regeneration energies as low as 2.1 GJ/tCO₂ are possible (compared with 2.8 GJ/tCO₂ in the previous review). Overall, the lack of further pilot-scale demonstration of fully integrated precipitating process suggests the TRL has not progressed significantly since the previous review.

Liquid–liquid phase-separating systems suggest greater potential for pilot-scale demonstration. While some systems certainly face challenges, such as the increased viscosity of the CO₂-rich phase, these systems have progressed to pilot-scale evaluation. In the previous IEAGHG review (2014) these systems were evaluated at TRL 4, with the potential to increase to TRL 5–6 if planned pilot-scale evaluation was undertaken. While some pilot-scale evaluation has now been realised (2-(diethylamino)ethanol/3-(methylamino)propylamine evaluation by SINTEF/NTNU), this has been achieved using a synthetic flue gas. Despite the cancellation of the previously planned pilot-scale demonstration on a power plant flue gas, the DMX process is planned for further evaluation treating a blast furnace gas. Should these technologies proceed to pilot-scale evaluation on real process gas streams, then there is the potential for further increase in the TRL. At the time of writing, however, these systems appear to be at a similar level of development as the previous review.

2.1.3 Ionic liquids

Ionic liquids are molten salts comprising organic cations with organic/inorganic anions that have melting points at or below room temperature (Bara 2016). The properties of the ionic liquid can be tailored through the choice of cation, anion and associated functional groups. They typically have low vapour pressures and large enthalpies of vaporisation. Their stability, and high CO₂ solubility and selectivity, makes them attractive as potential absorbents for PCC of CO₂ (Zhai and Rubin 2014). One of the challenges for ionic liquids when used for CO₂ capture is their high viscosity, which can reduce mass-transfer rates and limit application in standard absorption/desorption processes. The high viscosity can also reduce heat transfer rates, particularly on the rich side of the cross heat exchanger, when used in a standard liquid absorption process. Significant research is under way investigating methods for reducing viscosities through structural variations and blending with other, less viscous absorbents. However, even after blending, viscosity can still be an issue after absorption of CO₂. Ionic liquids have also been considered as a replacement for the water component of conventional capture absorbents (Lockwood 2016). For most ionic liquids, CO₂ capture is via physical absorption, and as such is highly dependent on CO₂ partial pressure and temperature. This can be challenging under the low CO₂ partial-pressure conditions of PCC, and thus methods to incorporate some form of chemical reactivity are being pursued (Bara 2016). Despite considerable research at laboratory scale, few ionic liquids have progressed to pilot-scale demonstration. Lockwood (2016) identified the primary challenges facing their deployment as their relatively high cost, and their generally high viscosity, which adds to energy consumption and limits mass transfer.

The Institute of Chemical Engineering, Polish Academy of Sciences, evaluated imidazolium-based ionic liquids ([Emim][AC], [Bmim][AC]) in a bench-scale packed column. Low liquid flow rates were required to avoid column flooding (Ziobrowski et al. 2016). Yasouj University evaluated imidazolium-based acetate ionic liquid for CO₂ capture in a bench-scale packed column at pressures above atmospheric. Viscosity issues were noted when operating at temperatures below 80 °C (Zareie-Kordshouli et al. 2017), and absorption pressures above 8 bar were recommended for a feasible process (Zareie-Kordshouli et al. 2018). Imidazolium-based room-temperature ionic liquids have also been evaluated by the University of Colorado at Boulder (Bara et al. 2009). Georgia Tech Research Corporation evaluated reversible ionic liquids for CO₂ capture applications. Hysys simulations suggested a regeneration-energy requirement of 1.5 GJ/tCO₂ (Eckert 2011). Ionic liquids have also been evaluated by the University of Notre Dame. They identified characteristics that increase CO₂ capacity, lower viscosity and can be used to tune the enthalpy of reaction. They identified an ionic liquid of interest, provided it could be produced at lower cost (Brennecke et al. 2012). Table 13 provides a summary of additional ionic liquids (or blends) that have progressed through to bench or pilot-scale demonstration of an integrated absorption/desorption process.

Table 13 Summary of ionic liquids (IL) evaluated for post-combustion capture of CO₂ at pilot scale

TECHNOLOGY COMPANY/RESEARCH INSTITUTE	DESCRIPTION	COST AND ENERGY INFORMATION	REFERENCES
IL/amine blend ION Engineering	Enhanced CO ₂ solubility of IL enhances absorption properties of MEA, enabling 99% CO ₂ capture. Initial IL developed substituted for 1-ethyl-3-methylimidazolium (Evonik) as a result of cost. Evaluated at National Carbon Capture Center. Unfortunately IL suffered degradation from amine used in blend.	CO ₂ -capture cost of 27 US\$/t and an increase in cost of electricity (COE) of 37% over a non-capture power plant was initially estimated.	Lockwood 2016 Bara 2016
MEA/IL National Centre for Scientific Research, Greece	IOLICAP project (European Union) evaluated several ionic liquids for CO ₂ capture. An IL blend with MEA was evaluated at pilot scale. MEA degradation rate observed to decrease (from 1.28 to 1.26 kg/d) after addition of IL.	Simulation results showed a 6% decrease in regeneration-energy requirement for MEA/IL blend compared with same plant using MEA only.	IOLICAP 2016

Zhai and Rubin (2014) evaluated the cost of a post-combustion CO₂ absorption plant using the ionic liquid trihexyl-(tetradecyl)phosphonium, 2-cyanopyrrolide for a 650-MW coal-fired power station. Absorption of CO₂ into the liquid was simulated using a multi-stage equilibrium-based modelling framework. A single-stage flash was used for absorbent regeneration, with energy requirement including the energy for solvent heating, enthalpy of reaction and water vaporisation (3.6 GJ/tCO₂). They estimated a CO₂-capture cost of \$62/tCO₂ (2011 USD) when capturing 90% CO₂. This is higher than the United States Department of Energy (US DOE) target of \$40/tCO₂, and was attributed to the high capital cost of the process. De Riva et al. (2017) simulated eight different ionic liquids for PCC. They found that in countries where electricity prices could be assumed to be lower, the cost of CO₂ capture using ionic liquids can approach the DOE target (de Riva et al. 2017).

Discussion on commercialisation potential and development since previous review

In the previous review, PCC using ionic liquids was assessed as having TRL of 1. While some pilot-plant work has progressed with amine-ionic-liquid blends, interest in this area appears to be declining. ION Engineering in particular are no longer progressing development of their ionic-liquid-based absorbent, and have moved on to other hybrid absorbents. The main challenges observed for ionic liquids when applied to PCC of CO₂ are much the same as identified in the previous review: cost and high viscosity. Additional challenges, such as degradation of the ionic liquid when blended with amines, have now also been identified. Most of the ongoing research in this area is at laboratory scale, evaluating properties of the absorbents.

It appears solutions have not yet been found for the challenges faced when working with these absorbents, which is making their use with conventional contacting equipment problematic. There is perhaps potential for applying these absorbents to other contacting devices, such as being incorporated into membranes, encapsulated or used with rotating packed beds, where viscosity is less of an issue and lower amounts of absorbent are required. As an absorption liquid applied to a standard contacting column, however, there appears to be minimal progress towards demonstration since the previous review. Though the results were not promising, ionic liquids reached a TRL of 4 through the pilot-scale evaluation completed by ION Engineering. The

challenges still remaining for this technology, however, suggest that the commercialisation potential is still low.

2.1.4 Non-amine, and non-aqueous (water-lean) absorbents

For conventional, amine-based PCC liquid absorbents, the largest component is water. This adds to the volume to be pumped around the system, and the sensible and latent heat required for regeneration. Researchers have considered replacing the water component of the absorbents as a means of reducing energy requirements and costs. The organic liquids often suggested have lower specific heats, which suggest decreases in reboiler duty are possible. A small fraction of water might be useful as stripping gas in the regeneration process, otherwise operation under vacuum might be necessary.

Piperazine-promoted, sterically hindered amines blended with ethanol have been evaluated at laboratory scale at Hacettepe University (Duatpepe et al. 2017). Additional non-aqueous absorbents being progressed for CO₂ capture are outlined in Table 14.

Table 14 Overview of non-amine and non-aqueous absorbents evaluated for post-combustion CO₂ capture

TECHNOLOGY COMPANY/RESEARCH INSTITUTE	DESCRIPTION	COST AND ENERGY INFORMATION	REFERENCES
Non-aqueous solvent (NAS) Research Triangle Institute (RTI) International	Hydrophobic diluent for amine blend with <10% water. Bench-scale evaluation completed to reduce solvent make-up cost, and reduce evaporative and degradation losses. Preliminary analysis indicates that the NAS process can reduce energy consumption by 30–50% compared with standard amine process. Reaction kinetics about 2 x slower than MEA. Evaluated for 100 h at lab-scale treating synthetic flue gas (2–8 kgCO ₂ /h). Long-term (~1600 h) evaluation completed at SINTEF’s Tiller pilot plant (60 kW _e) with regeneration energy 2.1–2.3 GJ/tCO ₂ . This process has now been selected for scale-up and evaluation at TCM (10 MW _e).	2–2.8 GJ/tCO ₂ (40% reduction compared with MEA), but at higher liquid-to-gas (L/G) ratio (8 kg/kg c.f. 3 kg/kg for MEA). Regeneration energy as low as 1.6–1.9 GJ/tCO ₂ under wet conditions. Further reduction expected with absorber intercoolers. Cost of CO ₂ avoided estimated at 73-80 \$/tCO ₂ . Cost of electricity (COE) 130 \$/MWh (c.f. 147 \$/MWh for MEA).	Zhou et al. 2018 Zhou et al. 2017 Tanthana et al. 2017
Amino-silicone molecule with organic co-solvent (e.g. triethylene glycol, TEG) GE	A mixture of a primary amino-silicone (GAP-1) with TEG was evaluated at the National Carbon Capture Center (NCCC). 66% capture of CO ₂ was achieved on the 0.5-MW _e pilot-scale unit using a continuously stirred-tank reactor desorption unit. Using a steam stripper desorption unit increased capture efficiency to 95%. Further work has focused on developing second-generation amino-silicones for CO ₂ capture. Secondary amino functional disiloxanes were found to have lower heats of absorption (in the range 2–2.2 MJ/kgCO ₂). In addition, amino-silicones that contain electron-donating ethylaminopropyl groups attached to the silicone core were found to display excellent CO ₂ uptake, and maintained a liquid, flowable state after reaction.	Heat of reaction 2.5–2.6 MJ/kgCO ₂ (c.f. MEA 1.9 MJ/kgCO ₂). Capture cost 51 \$/tCO ₂ (30% lower than MEA benchmark). 1.8% (HHV) gain over MEA process. Based on NCCC evaluation, CO ₂ -capture cost estimated between 46 and 53 \$/tCO ₂ (dependent on level of degradation). 20% reduction compared with MEA.	Perry et al. 2012 O’Brien et al. 2014 Perry 2016 Perry et al. 2017 Hancu 2017

TECHNOLOGY COMPANY/RESEARCH INSTITUTE	DESCRIPTION	COST AND ENERGY INFORMATION	REFERENCES
	GAP analysis identified solvent thermal degradation, thermal oxidation and hydrothermal equilibration as critical technology gaps to be addressed in future research & development.		
1-BEIPADIP-2-BOL Pacific Northwest National Laboratory	CO ₂ -binding organic liquids with polarity-swing-assisted regeneration (PSAR). PSAR maintains reboiler duty, but reduces temperature by destabilising CO ₂ carrier. Bench-scale continuous-flow evaluation. Liquid film mass-transfer coefficients comparable to aqueous solvents, CO ₂ capture >90% achieved (L/G >2 mol/mol). High rich-solvent viscosity found to negate benefits of PSAR.	~5 wt% water, heat of solution: 80 kJ/mol, current price \$15/kg. 900–1100 BTU/lb (based on simulation). 870 BTU/lb projected if viscosity can be limited to 20 cP. Where viscosity is 356 cP, capital costs are approx. double DOE case 10 (LCOE increase 115% over base plant with no capture). If viscosity can be maintained at 20 cP, capital costs approx. DOE case 10 (71% increase in LCOE over base plant).	Heldebrant 2017 Zheng et al. 2016
Carboxylic acid salt in organic media C-Capture (Spin-off from University of Leeds)	'Amine free' absorbent that reacts with CO ₂ to form carboxylate ester. Can be regenerated by heating or acidification similarly to amine-based processes. Evaluation at 1 tpd pilot-plant at Drax power station in the UK (biomass-enhanced CO ₂ capture and storage) is currently underway.		Patent US 2017 0001142 A1 C-Capture 2018

Discussion on commercialisation potential and development since previous review

Non-aqueous/non-amine absorbents were not covered in the previous review. While most ongoing work is currently at laboratory scale, a few absorbents have seen significant development. These include GE's amino-silicones, which have now been evaluated at the National Carbon Capture Center (NCCC), and Research Triangle Institute (RTI)'s evaluation on the Tiller pilot plant. However, there are still challenges associated with large-scale operation of GE's amino-silicone process. This suggests the technology has progressed to a TRL of 5, but with the potential for significant increase after the completion of RTI's process evaluation at TCM.

The base process of the non-aqueous and water-lean absorbents uses the same general plant layout as standard liquid-absorption-based PCC. This suggests that in general, scale-up of the technology should be relatively straightforward. The only potential issues are dependent on the specific absorbents. For example, amino-silicones can have volatility issues, leading to condensation and blockages in the stripping column overhead. The addition of triethylene glycol can reduce these issues, and there are other potential engineering solutions, but this makes the process more complicated.

2.1.5 Microencapsulation

Microencapsulation involves containing the absorbent liquid inside a thin, polymer shell, forming 100–600 µm beads with 10–50 µm wall thicknesses (Varicella et al. 2015). This process significantly increases the surface area for mass transfer, provided the shell is permeable to CO₂ and strong

enough to survive the operating conditions of the process. The increased surface area has the potential to reduce the height required for absorption. While mass transport across the capsule shell is slightly lower relative to neat liquid absorbents, the surface area enhancement gained provides an order of magnitude increase in CO₂ absorption rates for a given sorbent mass. Another advantage of encapsulation is the potential to use absorbents deemed challenging for conventional absorption systems. This includes absorbents with high viscosity (such as ionic liquids), high corrosivity, slow kinetics, or those that precipitate. The microcapsules combine the advantages of liquid absorbents (high capacity, high selectivity, water tolerance) and solid sorbents (high surface area, low volatility) (Vericella et al. 2015). Evaluation of microencapsulation is still at laboratory scale, with no technologies yet progressing to pilot-scale demonstration in this area. A summary of some of the ongoing research in this area is provided below.

Vericella et al. (2015) used a silicone material for the shell, encapsulating solutions of potassium and sodium carbonate. The CO₂ permeability of the shell was found to be high (3,260 barrer), and showed no noticeable decrease in permeability after exposure to temperatures up to 150 °C. The microcapsules were cycled between CO₂ absorption and desorption conditions, showing no decrease in permeability, and continued fast uptake of CO₂ (<1 min) over 80 cycles. The capsules were found to be permeable to water, quickly reaching osmotic equilibrium with their surroundings. Thus, their CO₂ absorption capacity will likely not be decreased due to the presence of water in flue gas, unlike the case with many solid sorbents. The rate of CO₂ absorption was increased more than 10 fold, and precipitates successfully contained. Stolaroff et al. (2017) have also shown that CO₂ mass-transfer rates were significantly enhanced by microencapsulation.

Rakasjati et al. (2017) completed a preliminary techno-economic assessment of an encapsulated 30 wt% MEA system using fixed-bed, fluidised-bed (absorber), and bubbling fluidised-bed (regenerator) reactors. No heat transfer was used between the rich and lean absorbent streams. Where fixed beds were used, multiple beds were required to maintain velocities below the fluidisation velocity. This led to capital costs double that of a standard 30 wt% MEA process using conventional packed columns. Bhattacharyya et al. (2017) similarly determined that fixed-bed contactors were not suitable for use with encapsulated carbonate solutions in their simulation. Rakasjati et al. (2017) also found high capital costs for the case using fluidised-bed reactors. This was due to the large tubes required for heat transfer within the beds. The heat duty of both encapsulated systems was also found to be significantly higher than required for a conventional absorption system. This perhaps highlights that encapsulation is better suited to more novel absorbents that, due to their properties, cannot be used in conventional contacting systems. This is the focus of an ongoing DOE-sponsored research program in which the University of Notre Dame, in collaboration with Lawrence Livermore National Laboratory, are evaluating hybrid encapsulated ionic liquid and/or phase-change ionic liquid materials for PCC (McCready et al. 2018).

In a subsequent theoretical analysis of the effect of absorbent properties on overall system cost, Rakasjati et al. (2018) noted that increasing the permeability of the capsule shell did not have a significant impact on cost. In contrast, minimising the capsule shell thickness had a much more significant effect.

[Discussion on commercialisation potential and development since previous review](#)

In the previous review, encapsulated systems were at an early stage of development, and were given a TRL of 1. Research completed since then has been at laboratory scale, with no large bench

or pilot-scale demonstration yet reported. The ongoing laboratory-scale evaluation of micro-encapsulated absorbents suggests this technology has now progressed to a TRL of 2–3.

One of the challenges with this system is scale-up of the fabrication system to produce the volume of capsules required for a larger system. Maintaining the quality of the capsules as the fabrication system is scaled up is also challenging. In the previous review, it was also noted that these systems were still to be evaluated on real flue gases, and as such, their resistance to other flue-gas components is not yet known. Incorporation of encapsulated absorbents into CO₂ capture processes so far has focused on fluidised bed systems. As such, challenges facing fluidised bed reactors will also be challenges for encapsulated systems. These include the mechanical integrity of the capsules and potential for attrition.

2.1.6 Amino acid and other mixed-salt absorbents

Amino-acid and mixed-salt processes have been identified as attractive absorbents for PCC due to their low toxicity, higher biodegradability than conventional amines, low volatility, and for some, a high resistance to oxidative degradation (Sanchez-Fernandez et al. 2013). Amino acids have found use in other industries, such as BASF’s Alkazid process developed for the removal of H₂S or CO₂ from refinery gases. For PCC applications, one of the more developed amino-acid processes is the Siemens PostCap process. Other well-known, salt-based processes include NH₃ and potassium carbonate, such as UNO Technology’s promoted K₂CO₃ process (see precipitating absorbents). Combining salt solutions can overcome some of the challenges faced when using individual salt solutions, such as the low reaction rate of K₂CO₃ solutions under PCC conditions. Some of these processes have now progressed to pilot-scale evaluation, and are summarised in Table 15. A flow diagram of SRI International’s mixed salt process is provided in Figure 7.

Table 15 Summary of amino-acid and other mixed-salt processes for post-combustion CO₂ capture

TECHNOLOGY COMPANY/RESEARCH INSTITUTE	DESCRIPTION	COST AND ENERGY INFORMATION	REFERENCES
Mixed-salt process SRI International	Ammonium and potassium carbonate salts. Combining salt solutions removes some of the issues faced with individual salts. Uses selective regeneration producing NH ₃ -rich and K-rich solutions. K-rich solution returned to top of absorber, NH ₃ -rich to base. This allows capture of NH ₃ slip in the K-rich section, resulting in low NH ₃ emissions. Regeneration can be completed at higher pressure (10–40 bar, >160 °C). Heat of reaction 40–50 kJ/mol, 30–40 wt% mixed salt. Overall CO ₂ absorption rate comparable to 30 wt% MEA. Operated at pilot scale (0.25–1 t/d) for 1.5 yrs. No absorbent chilling required (absorber 20–40 °C to avoid solids formation). Technology has been selected for evaluation at TCM (10 MW _e).	Simulated for 550 MW power plant (US DOE case 12). Suggest regeneration energy 2 GJ/tCO ₂ (regen. pressure 10 bar). Auxiliary power requirement 20% of MEA process. Cost of electricity 117.4 \$/MWh (c.f. DOE case 12 MEA 133.2 \$/MWh). Cost of CO ₂ capture (excluding transport & storage) ~38 \$/tCO ₂ (c.f. DOE case 12 MEA 54 \$/tCO ₂).	Jayaweera 2017 Jayaweera et al. 2017 Jayaweera et al. 2016
PostCap Siemens	9,000 h pilot-scale operation achieved, 6,000 treating coal flue gas, 3,000 h treating natural-gas flue gas. Total solvent loss per year due	2.5–3 GJ/tCO ₂	Melcher et al. 2014 Horn et al. 2015 Reichl et al. 2014 PostCap 2015

TECHNOLOGY COMPANY/RESEARCH INSTITUTE	DESCRIPTION	COST AND ENERGY INFORMATION	REFERENCES
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to degradation estimated to be less than 20 % of the amount seen in standard MEA process.

Kuettel et al. 2013

Captures both SO₂ and CO₂ from flue gas. CO₂ removed from absorbent via thermal stripping, absorbed S removed via crystallisation (uses belt filter and centrifuge). As amine absorbents are non-volatile, standard thermal reclamation not possible. Crystallisation process developed for this purpose.

Have completed feasibility studies and front-end engineering design for several large-scale PCC applications, and technology qualification program for Carbon Capture Mongstad project.

CASPER TNO	Uses a potassium salt of an amino acid for combined removal of SO ₂ and CO ₂ . Developed as part of iCap project. CO ₂ removed via thermal stripping, SO ₂ removed via precipitation. Model amino-acid (β-alanine) evaluated at pilot-scale. Conversion of absorbed sulfite to sulfate determined to be rate limiting.	CSIRO evaluated concept for brown-coal-fired power station. 10–20% reduction in cost of CO ₂ avoided compared with standard plant (30 wt% MEA with flue-gas desulfurisation)	Cousins et al. 2014 iCAP 2013
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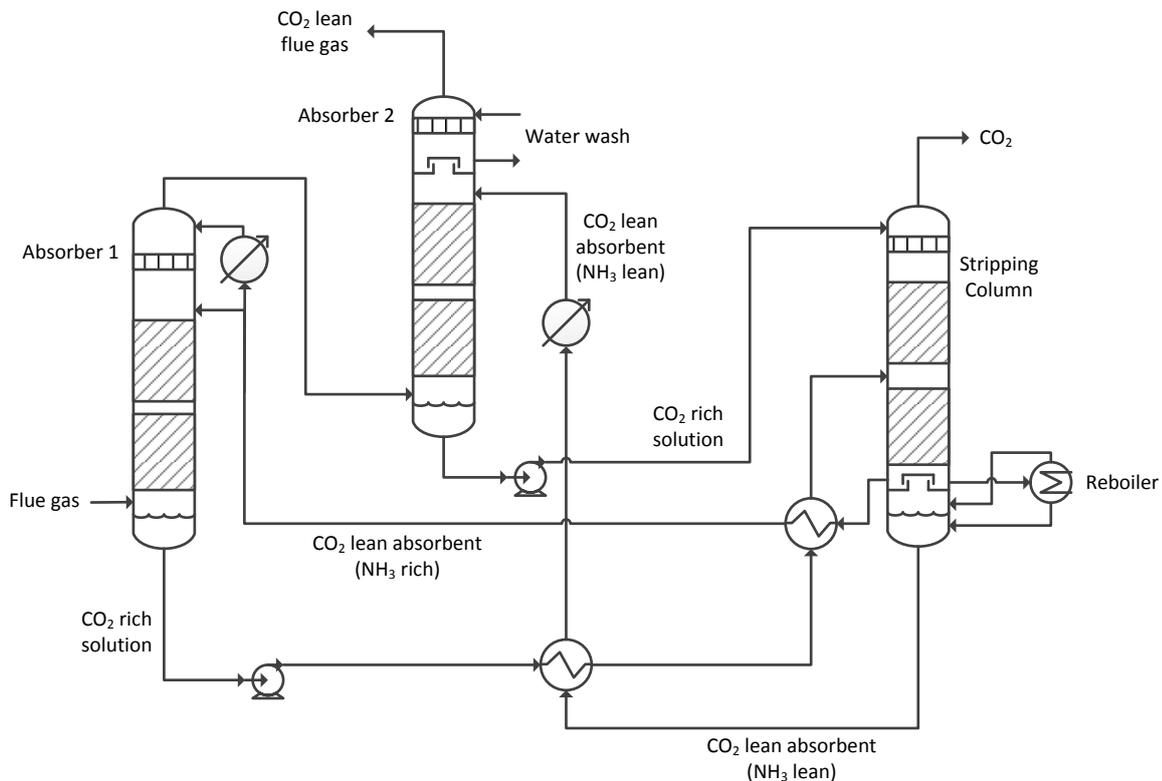


Figure 7 Flow diagram of SRI International's mixed salt process (Jayaweera et al. 2017)

Discussion on commercialisation potential and development since previous review

Amino acids for PCC do not appear to be covered in the previous review, but have reached a TRL of 6 with pilot-scale demonstration by Siemens. On the whole, amino-acid and mixed-salt processes

use a similar layout to standard liquid-absorption-based capture. This suggests scale-up of these technologies should be fairly straightforward. A possible issue for these technologies is the potential for unwanted precipitation. SRI's mixed salt absorber operates at 20-40 °C to avoid solids formation. For both the Siemens and TNO processes, precipitation is used to remove a solid by-product. Care will need to be taken to ensure unwanted precipitation does not occur in other parts of the process.

Siemens also raised a potential issue with regeneration of the absorbent. Due to the properties of amino acids (low volatility), they do not lend themselves to the traditional thermal reclamation methods. Instead, Siemens have developed a new precipitation method for reclamation, which has been evaluated at pilot scale. Siemens have currently halted progress of their technology due to lack of market interest.

Elements of TNO's CASPER process have been evaluated at pilot scale; however, the regeneration was completed offline. It does not appear to have achieved fully integrated pilot-scale demonstration at this stage.

SRI's mixed-salt process has received funding for evaluation at 10-MW_e scale at TCM, suggesting it could progress to TRL 7. Another attraction of the mixed-salt process is that it does not degrade, unlike conventional amines. This will simplify scale-up of this process, as extended operation is not required for the purpose of determining absorbent degradation rates.

2.1.7 Catalysts and other activators

Some absorbents developed for PCC of CO₂ have the potential for lower regeneration-energy requirements, but suffer lower mass-transfer rates, with the overall economics not being attractive. One method for improving the economics is to add a catalyst or other activator to enhance the CO₂ absorption and/or desorption reaction rates. A new approach is to add a biocatalyst or enzyme, carbonic anhydrase (CA), to the CO₂ capture absorbent. CA regulates CO₂ levels in the cells of most organisms by catalysing reversible CO₂ hydration to H₂CO₃. Genetic modification of CA makes it possible to use it in combination with aqueous alkanolamine solutions within an industrial environment (Penders-van Elk and Versteeg 2016). Genetically modified, temperature-resistant strains have been developed by companies such as Novozymes, Codexis and CO₂ Solutions (Lockwood 2016). Where the initial dissolution of CO₂ into the capture absorbent is the rate-limiting step, CA can accelerate the kinetics (Lockwood 2016). This was highlighted by work from SINTEF evaluating CA addition to MEA and methyl-diethanolamine (MDEA) solutions in combination with membranes in a laboratory-scale membrane contactor treating a synthetic flue gas. CO₂ absorption rate was enhanced for MDEA with the addition of 1 wt% enzyme. No enhancement was observed for 30 wt% MEA (Kim et al. 2017).

The Technical University of Denmark have also evaluated CA addition to MDEA solutions. They completed laboratory pilot-scale analysis of the blend treating a synthetic flue gas. Regeneration was completed at low temperature with air stripping. CA was noted to increase reaction rate, with higher mass transfer observed at 28 °C compared with 40 °C (Gladis et al. 2017).

The Technical University of Dortmund have evaluated the addition of CA to reactive liquid absorbents as part of the European Union (EU) InterAct project (InterAct 2017). Mass-transfer characteristics were evaluated in wetted-wall and laboratory spray reactors, with the most promising blends evaluated in a pilot-scale packed absorber (Kunze et al. 2015). This work

progressed to pilot-scale evaluation of CA-enhanced MDEA solutions, with the enzyme in both dissolved and immobilised forms (Leimbrink et al. 2017, Leimbrink et al. 2018).

To overcome the instability of CA in industrial applications, Lawrence Livermore National Laboratory has evaluated synthetic analogues that mimic the active site of the enzyme. Two such molecules developed include 1,4,7,10-tetraazacyclododecane and 1,5,9-triazacyclododecane. Both are completed with a Zn(II) ion. N atoms in these cyclic molecules mimic the imidazole nitrogens of the CA active site (Wong et al. 2011, Lau et al. 2013). The University of Kentucky has also evaluated CA analogues. These were evaluated in a 0.1 MW_{th} test unit and found to increase mass transfer of the catalysed absorbent by 40% (Lippert et al. 2013, Lippert et al. 2014).

Other additives considered for enhancing CO₂ capture reactions include metal ions, amines (such as PZ), amino acids and other chemical additives, such as hypochlorite (Penders-van Elk and Versteeg 2016). The CO₂CRC, for example, added glycine to their K₂CO₃ process to enhance CO₂ absorption rates, though addition of the catalyst was noted to require the addition of anti-foam. The University of Regina evaluated adding inorganic catalysts, including alumina spheres and the zeolite HSM-5. This allowed regeneration to be carried out at temperatures below 100 °C, with regeneration energies of 1.5 GJ/tCO₂ estimated (Shi et al. 2014). Shinshu University has evaluated adding functionalised alumina particles to rich DEA solutions. Particles functionalised with acidic functional groups were found to enhance CO₂ absorption (Takahashi et al. 2017). The CSIRO evaluated the addition of metal-ion catalysts to aqueous-amine absorbents. This uses the ability of amines to react with CO₂ and form complexes with transition metal ions (Cu(II)) to reduce the heat of CO₂ desorption via metal-amine complexation. Adding metal ions improved CO₂ capture performance via mitigating the absorption-based temperature increase, enhancing desorption rates and increasing solvent cyclic capacity. The heat of CO₂ desorption was noted to decrease by 13–24% (depending on Cu ion concentration) (Li et al. 2018).

By far the most researched catalyst for enhancing CO₂ capture is the addition of the enzyme CA. A summary of more developed systems is provided in Table 16.

Table 16 Summary of technologies incorporating catalysts and/or activators for post-combustion CO₂ capture

TECHNOLOGY COMPANY/RESEARCH INSTITUTE	DESCRIPTION	COST AND ENERGY INFORMATION	REFERENCES
Immobilised enzyme biocatalyst in combination with alkali salt solution (K ₂ CO ₃ and proprietary blend AKM24) Akermin	Polymer added to absorber packing then impregnated with enzyme. Delivers enzyme to gas-liquid interface in absorber, and prevents enzyme from seeing high T conditions in stripper. Evaluated at bench scale at National Carbon Capture Center (NCCC). Long-term evaluation (~3400 h) showed high stability of the enzyme in both K ₂ CO ₃ and AKM24 (80% capture). Second-generation system used biocatalyst micro-particles. It was assumed that a particle-separation system is available upstream of the stripper to prevent the biocatalyst particles from entering the high-temperature stripper (105 °C).	Simulation estimates second-generation system with atm P reboiler (105 °C) 42% lower equivalent work compared with MEA base case. 34% reduction in incremental cost of electricity compared with 30 wt% MEA (DOE case 12). Operating stripper under vacuum at 80 °C, with catalyst particles able to circulate through the lower-temperature column, calculated to have incremental cost of electricity 31% lower than the MEA base case.	Reardon et al. 2014

TECHNOLOGY COMPANY/RESEARCH INSTITUTE	DESCRIPTION	COST AND ENERGY INFORMATION	REFERENCES
	In 2016, CO ₂ Solutions purchased several assets from Akermin, followed by Akermin ceasing operation and liquidating assets.		
Carbonic anhydrase enzyme enhanced absorbent (K ₂ CO ₃) with vacuum regeneration Novozymes Doosan University of Kentucky Pacific Northwest National Laboratory	Regeneration under vacuum (temp <80 °C). Low temperature avoids enzyme degradation, but adds to compression load. 500 h operation of bench-scale unit with synthetic flue gas (23.5 wt% K ₂ CO ₃ , 2.5 g/L enzyme). 84% CO ₂ capture achieved with 20% enzyme replenishment rate per ~7 h steady-state period. Presence of dissolved enzyme in stripper caused foaming. Controlled with anti-foaming agent. Concerns expressed regarding availability of vacuum generation at power plant scale.	Final CO ₂ capture costs were not competitive unless enzyme longevity could be significantly improved. Cost of electricity (COE) determined to be 9% higher than DOE case 10 (30 wt% MEA). 2.8% improvement achieved over DOE case 10 if enzyme longevity improved and additional power output from very low-pressure turbine assumed.	Lockwood 2016 Salmon et al. 2015
Proprietary enzyme (1T1) with K ₂ CO ₃ CO ₂ Solutions	10 t/d facility with free-flowing enzyme. Regeneration at 80–95 °C using low-grade heat. 2500 pilot-scale operation at natural-gas-fired boiler in 2015. The low-volatility absorbent resulted in high-purity CO ₂ product (>99%), with the main contaminants being O ₂ and N ₂ from air ingress. No degradation of the absorbent was observed during the campaign, and no absorbent top-up was required (solvent bleed is expected to be required when treating flue gases containing NO _x and SO _x). CO ₂ Solutions first commercial plant was announced in August 2016. A 30 tCO ₂ /d plant will be installed on the boiler of a pulp mill, with the CO ₂ piped 1 km for use in vegetable greenhouses. Commissioning of the plant was expected in the 4th quarter of 2018.	3.8 GJ/tCO ₂ Capture cost 39 \$/tCO ₂ based on pilot-plant results	CO ₂ Solutions 2017 Fradette et al. 2017 Lockwood 2016

Discussion on commercialisation potential and development since previous review

Enzyme-catalysed absorption was covered in the previous review (IEAGHG 2014). As work developing suitable enzymes was at proof-of-concept stage, this process was evaluated as being at a TRL of 1. Since then, enzyme-catalysed CO₂ capture has seen significant demonstration, particularly that achieved by CO₂ Solutions, suggesting this technology is at a TRL of 6. More novel technologies using synthetic analogues, or combining the enzymes into amine solutions, are at a lower level of development.

One potential challenge for widespread deployment of enzyme-based capture could be the production of sufficient enzyme. CO₂ Solutions believe this is not a significant challenge, given they have already prepared batches of enzyme at the scale required for their pilot and demonstration plant. The CO₂ Solutions process uses a similar plant layout to standard liquid-absorption-based CO₂ capture, with the enzyme free flowing in the absorbent liquid. This suggests

scale-up of this technology should be relatively straightforward. Other technologies, where the enzyme is immobilised or removed from solution, would provide additional challenges. During the EU InterAct project, Novozymes assessed the different methods for incorporating the enzyme (packing, filtration) and determined these technologies to be at a TRL of 1–3. Additional challenges for enzyme based capture include the stability and longevity of the enzyme. Low lifetime rates requiring significant fresh enzyme addition can lead to a capture process being uneconomic. As thermal stability can be an issue, regeneration of the absorbent is often achieved under vacuum at temperatures < 100°C where the enzyme is free-flowing.

2.1.8 Combined capture concepts

For most PCC applications, the CO₂ capture facility requires upstream pre-treatment of the flue gas. This is to lower the temperature (to typically 40 °C), remove particulate, and remove other acid components (e.g. SO₂) from the flue gas. Even though they are present in much lower concentrations than CO₂, the other acid components will bind much more strongly to the amine and form a stronger acid than absorbed CO₂. Existing sulfur-removal technologies (e.g. limestone-slurry-based flue-gas desulfurisation, FGD) will likely require upgrading, or an additional polishing step, to meet the more stringent allowable SO₂ concentrations entering PCC facilities. As such, if the CO₂ and SO₂ removal steps can be combined, there is potential for significant cost savings. This is of particular importance in countries such as Australia, where FGD is not currently employed in coal-fired power stations.

Potassium carbonate and NH₃ processes (e.g. UNO Technology, GE CAP) have the potential to remove both SO₂ and NO_x components from the flue-gas stream in addition to CO₂, forming sulfate and nitrate salt by-products. Both of these processes have been discussed previously. CSIRO have evaluated an advanced ammonia process linking the SO₂ removal and absorber wash stages. Simulations suggest the advanced process reduced energy consumption compared with a standard MEA plant by 20%, and capital cost by 7%, resulting in CO₂-avoided cost of USD\$53.2/tCO₂ (Li et al. 2016). This process is currently undergoing pilot-scale evaluation in Australia.

Amino-acid processes, such as Siemens' PostCap and TNO's CASPER processes, will similarly capture both the CO₂ and SO₂ from the flue gas. Both of these processes have now been evaluated at pilot scale, with absorbed sulfur removed from the sorbent via a crystallisation process. These technologies have been covered in the amino-acid section of this report. An economic analysis of the CASPER process applied to an Australian coal-fired power station was completed by CSIRO. This found 10–20% reduction in the cost of CO₂ avoided (dependent on power plant size) compared with a standard plant using FGD with CO₂ capture via 30 wt% MEA (Cousins et al. 2014).

Amine-based technologies include the Shell Cansolv process. Here, a first aqueous-amine absorbent is used to capture SO₂ from the flue gas, with a second amine used to capture the CO₂. Heat integration between the SO₂ and CO₂ absorbent regenerators is applied. CSIRO has also developed a combined capture concept using a single amine absorbent. This process, CS-CAP, is expected to have potential cost savings of \$100–\$200m over standard PCC due to avoidance of FGD (Pearson et al. 2017).

Discussion on commercialisation potential and development since previous review

Combined capture concepts were not covered in the previous review. Some of these concepts are at an advanced stage of development, such as the Shell Cansolv process employed at Boundary Dam. Siemens' PostCap process has also achieved significant pilot-scale demonstration, suggesting these technologies are at a TRL of 6 or above. While aspects of the CASPER process were evaluated at pilot scale, regeneration was performed offline at this stage, suggesting a TRL of 4. The CS-CAP process is still under development, with laboratory-scale evaluation currently under way.

Sulfur removed from the flue gas in the Shell Cansolv process is converted to H_2SO_4 . For the Siemens' process it is unclear what will happen with the sulfate removed from the process. In the economic evaluation of the CASPER process, it was assumed that the K_2SO_4 produced could be sold. This cost was assumed to cover the costs of separating the precipitate and any purification requirements. It is unknown whether the assumption of being able to sell sulfates produced from a CO_2 -capture process is valid at this stage.

In general, the combined capture processes follow the same plant layout as standard liquid-absorption-based PCC, suggesting straightforward scale-up of the process. The methods suggested for removing the sulfur by-product from solution are currently based on commercially available equipment (mixing tanks and filtration). While some of these processes are at a high level of development, others still require demonstration of the fully integrated process.

2.2 Membranes

Membranes are a thin barrier over which one species is more mobile than others present in a gas mixture. The partial pressure difference across the membrane provides the driving force for separation. CO_2 removal from flue gases is challenging due to the low CO_2 partial pressure and presence of water vapour (Sandru et al. 2013). Membranes are attractive for PCC of CO_2 , due to their low energy requirement and modular nature making them more amenable to stepwise scale-up. In the reported PCC applications, membranes are used to separate CO_2 from a gas mixture, or as part of a process concept to enrich combustion air or flue gas with CO_2 , thereby increasing the efficiency of the downstream CO_2 -capture process. In some instances the membranes are also used as the contacting device, providing the surface area for mass transfer. Here absorbent flows down one side of the membrane, while the gas flows up the other. Membranes can be arranged in a plate and frame structure, as spiral-wound modules, or as hollow fibres. Hollow-fibre configurations dominate current industrial applications, due to their high packing density and comparatively lower cost (Abanades et al. 2015).

Where membranes are porous, separation can be on the basis of molecular size (microporous) or Knudsen diffusion (mesoporous). For dense (non-porous) membranes, the gas species dissolves in the polymer before diffusing to the lower partial-pressure side (Baker 2012). Increasing permeance can be achieved by developing thinner membranes. For a membrane process to be economically attractive, permeance >1000 gas permeation units (GPU), and CO_2/N_2 selectivity >30 are suggested (Venna 2017). For a low-pressure, single-flue-gas membrane configuration, high-selectivity (>50 to 200) membranes are not considered a priority, since there is limited benefit in the cost of electricity reduction (Merkel et al. 2010). As a result, CO_2 product streams are typically

60% purity, and thus most membrane-based CO₂ capture processes will require a CO₂ compression and purification unit to meet higher CO₂ product gas purity specifications.

Membranes can be organic or inorganic. Inorganic membranes are attractive due to their temperature stability, resistance towards absorbents, well-defined and stable pore structure, and potential for sterilisation (Abanades et al. 2015). Porous, inorganic membranes evaluated for PCC applications include zeolites, mesoporous silica, carbon molecular sieves and metal organic frameworks (MOFs). However, inorganic membranes are usually more expensive and difficult to manufacture compared with polymeric membranes, and this has limited their application for PCC CO₂ removal.

Most membranes evaluated for PCC have been polymeric in nature. The low cost and versatility of fabrication and design of polymeric membranes make them attractive for large-scale PCC applications. Polymeric membranes, however, can suffer from ageing, where the polymer permeability decreases with time. Sorption of flue-gas components (such as CO₂ or H₂O) can cause some membrane materials to swell, decreasing selectivity. Polymer materials studied for PCC applications include polyimides, polysulfonanes, poly carbonates, cellulose acetate and polyethylene oxide. Membranes are often fabricated as a composite material, with a thin, selective membrane layer coated onto a porous support layer. Membrane Technology and Research (MTR) and the State University of New York at Buffalo are investigating isoporous supports that have a higher surface porosity than standard supports. These are anticipated to improve membrane permeance, reducing the required membrane area (NETL 2018b).

To avoid crystallisation of polymeric membranes, block copolymers can be used, consisting of alternating polymer chains (Lockwood 2016). Alternatively, the membrane can be used as a support for a CO₂ absorbent held within the pores of the membrane, known as a supported liquid membrane. The principal challenge for supported liquid membranes is maintaining their stability over long-term operation in flue-gas conditions, and vaporisation losses, particularly on the low-pressure permeate side (Lockwood 2016). Stability issues have limited the development of supported liquid membranes to date.

Standard membrane systems suffer a trade-off between permeability and selectivity. Mixed matrix membranes, where nanometre-sized inorganic fillers are dispersed in the polymer matrix, potentially provide a solution to the trade-off issues of polymeric membranes. The increased affinity of the particles for CO₂ can promote passage of CO₂ through the membrane. Breaking up tightly packed polymer chains can improve diffusivity and improve thermal and mechanical resistance (Lockwood 2016). To be cost competitive, it is likely that fabrication of mixed matrix membranes will need to use existing polymeric membrane manufacturing methods. Challenges of mixed matrix membranes include stability over time, even dispersion at high filler contents, and adhesion between heterogeneous phases (Dong et al. 2013, Abanades et al. 2015).

SINTEF has evaluated amino-functionalised, polyhedral, oligomeric, silsesquioxane nanoparticles dispersed in a polyvinyl-alcohol matrix for the selective separation of CO₂ from gas mixtures. Permeance and selectivity increased with the addition of amine-functionalised particles, but performance levelled off after further increases. CO₂ permeance was noted to decrease when SO₂ was introduced to the gas mixture (up to 400 ppm), thought to be due to a corresponding decrease in humidity as a result of the addition. The membrane was noted to recover after removal of SO₂ (Guerrero et al. 2017). Imperial College have developed a metal organic framework (MOF) exhibiting

photoresponsive absorption of CO₂. The MOF was incorporated as a filler into a mixed matrix membrane. Adding 5 wt% of the MOF was noted to increase the permeability of a PIM-1 membrane from 4000 to 6700 barrer (Prasteya and Ladewig 2018). Mixed matrix membranes were evaluated for post and pre-combustion capture as part of the EU M4CO₂ project (Energy efficient MOF-based mixed matrix membranes for CO₂ capture). Two prototype membranes were scaled up and developed into hollow-fibre membranes. Preliminary techno-economic assessment suggested CO₂-capture costs of 33 €/tCO₂. Lifecycle assessment showed the environmental impacts of a membrane-based system to be less than a comparable MEA-based CO₂-capture plant (M4CO₂ 2018). Combining the 'best' polymer with 'best' filler does not necessarily lead to the 'best' mixed matrix membrane. There are a large number of possible combinations, and the properties of the combined system require evaluation. Budhathoki et al. (2017) used a computational screening method to identify promising combinations, and completed a basic cost comparison in Aspen. They showed adding some MOFs to a membrane increased the cost of the CO₂-capture plant. Where favourable pairings could be found, they predicted a potential CO₂-capture cost of \$46–61/tCO₂.

Chemical modification of the inorganic fillers in mixed matrix membranes can also enhance separation properties through the integration of functionalised nanoparticles that exhibit facilitated transport properties (Guerrero et al. 2017), resulting in facilitated transport, or fixed site carrier membranes. Fixed site carrier membranes containing amino groups can work well with humidified flue-gas streams due to the reversible reaction mechanism of CO₂ with amino groups in the presence of water (Sandru et al. 2013). These membranes combine the durability of a solid polymeric membrane with the selectivity of a supported liquid membrane, without the limitation of washout of the carrier solution over time. CO₂ molecules are transported via facilitated transport and solution diffusion, while non-reactive gases such as N₂ are transported only via a solution-diffusion mechanism (Sandru et al. 2013).

The EU NANOMEMC2 project, led by the University of Bologna, are developing facilitated transport membranes incorporating graphene-based nanosheets and cellulose nanofibers. Graphene additions below 1 wt% were found to provide optimal performance (Rea et al. 2018, De Angelis et al. 2018). The University of South Carolina have developed ultrathin graphene-oxide (GO) membranes for CO₂ capture. These are prepared from single-layer GO flakes, and have been shown to have CO₂ permeance of 1000 GPU and CO₂/N₂ selectivities >600 (Zhou et al. 2017, Li et al. 2013). This work is continuing in a DOE-funded project in collaboration with the Gas Technology Institute (GTI), Rensselaer Polytechnic Institute and Ohio State University, evaluating two ultrathin GO-based membranes for CO₂ capture (Li and Yu 2018). Monash University are developing thermally rearranged polymers incorporating GO nanosheets. They have been able to achieve CO₂ permeance of 1780 GPU and CO₂/N₂ selectivity of 17 (Kim et al. 2018). The University of Melbourne are progressing the development of ultrathin composite membranes via the continuous assembly of polymer nano-coating technology (Kim et al. 2016). A range of composite membranes have been evaluated, with polymer-on-MOF architecture achieving CO₂ permeance >3000 GPU, and a CO₂/N₂ selectivity of 34 (Xie et al. 2018).

Membranes are receiving significant attention, research and development for their potential to reduce the cost of PCC. Much of this development has been at laboratory scale, separating CO₂ from pure N₂/CO₂ gas mixtures. Field testing with real industrial gases is crucial for membrane development. This encompasses the range of minor components present in flue-gas streams that

are difficult to replicate in laboratory environments, in addition to the effects of start-up, shut-down and other dynamic variances that occur in an operating facility. A review of membrane technologies assessed for PCC applications, with a particular focus on those evaluated at pilot scale, is provided in Table 17.

Table 17 Summary of membrane technologies evaluated at pilot scale for post-combustion CO₂ capture

TECHNOLOGY COMPANY/RESEARCH INSTITUTE	DESCRIPTION	COST AND ENERGY INFORMATION	REFERENCES
Polaris CO ₂ -selective polymeric membrane Membrane Technologies Research (MTR)	<p>Polaris membrane has active polymeric separation layer coated on an ultrafiltration membrane cast on a non-woven support layer. Gen-1 Polaris membrane has permeance of 1000 GPU, CO₂/N₂ selectivity 50. Gen-2 membrane has permeance of 2000 GPU, CO₂/N₂ selectivity 49. Commercial membrane prepared on large-scale roll-to-roll equipment.</p> <p>1 t/d spiral-wound module evaluated at the National Carbon Capture Centre (NCCC) (0.2 m diameter x 1 m length). High-flux Polaris membrane used in first step, sweep module with high-selectivity membrane used in second step. 1100 h operation (slipstream test with no CO₂ recycle). 85–90% CO₂ capture achieved. Membrane module recovered well after periods of power plant outage. Further evaluation confirmed long-term stability of membrane. 89% CO₂ capture achieved after 2200 h operation. 11,000 h total operation achieved on 1 t/d membrane module.</p> <p>Low-pressure drop plate and frame sweep module integrated into 20 t/d facility and evaluated at Babcock and Wilcox’s 0.6-MW_e coal-fired research boiler. 1500 h pilot-scale evaluation of integrated system achieved. CO₂ recycle noted to lower O₂ into boiler. Resulted in linear decrease in plant efficiency. 18% O₂ determined optimum for retrofit (based on simulation). Total heat absorption of furnace slightly reduced due to CO₂ recycle.</p> <p>Modest selectivity (~50) of membrane considered optimal. Focus on increasing permeance to reduce membrane area required.</p> <p>This technology has been selected for evaluation at Technology Centre Mongstad (TCM) (10 MW_e). Also completing design for large pilot (200 tCO₂/d) focusing on partial capture to be installed at coal-fired power plant operated by NRG Energy.</p>	<p>In National Energy Technology Laboratory ‘pathways project’, cost of various MTR configurations investigated. First year cost of electricity between \$81–88/MWh estimated (c.f. \$95–100/MWh for 30 wt% MEA).</p> <p>Economic analysis showed 90% capture could be achieved at lower cost than conventional process. Costs decrease significantly if capture % requirement is relaxed. Depending on process design, a minimum capture cost achieved at 30–60% capture (~\$35/tCO₂).</p> <p>Initial Gen 1 Polaris membrane cost produced at lab scale ~\$500/m². This was reduced to ~\$200/m² during project DE-FE0005795.</p> <p>Techno-economic assessment (TEA) based on results achieved at pilot plant. Membrane process achieved slightly higher power plant efficiency (28.6%) c.f. conventional amine process (Department of Energy (DOE) case 12 MEA, 28.4%). Total cost of electricity (COE) \$132.3/MWh (c.f. \$137.3/MWh for case 12 MEA), cost of CO₂ capture \$52/t (c.f. \$56.5/t for DOE case 12 MEA).</p>	<p>Merkel et al. 2016 White et al. 2015 White et al. 2017 Keairns et al. 2012 Kniep et al. 2018 Freeman et al. 2016 NETL 2018e NETL 2018f NETL 2018g</p>
PolyActive thin-film composite membrane Helmholtz-Zentrum Geesthacht Forschungszentrum Jülich	<p>PolyActive block co-polymer membrane of polyethylene oxide soft blocks and rigid blocks of poly-butylene terephthalate.</p> <p>11 m² module employed to enrich CO₂ concentration in flue gas from gas-fired central heating system (flue gas used for bioreactor). CO₂ purity in permeate calculated to be 47%. Membrane unit operated intermittently as required to supply CO₂ enriched gas to buffer tank. 1300 h operation, including 700 start-ups, achieved by 2014.</p>		<p>Pohlmann et al. 2016 Wolff et al. 2015</p>

TECHNOLOGY COMPANY/RESEARCH INSTITUTE	DESCRIPTION	COST AND ENERGY INFORMATION	REFERENCES
	<p>Evaluated as part of the METPORE II project. 9.8–12.5 m² envelope membrane modules evaluated for 740 h at coal-fired power plant. Flue gas compressed, cooled for water removal, and then reheated to avoid condensation.</p> <p>Membrane module found to respond well to transient operation. CO₂ purity of 68 mol% and CO₂ recovery of 43% achieved in single stage.</p>		
<p>Evaluated two commercial membranes: (1) hollow-fibre Air Products PRISM PA1020 polysulfone membrane module (2) spiral-wound Dow Filmtec NF3838/30FF polyamide membrane module</p> <p>University of Melbourne</p>	<p>Evaluated commercially available membranes on coal flue gas.</p> <p>Air Products PRISM module used asymmetric, glassy polymer fibres initially designed for air separation. CO₂ permeance and selectivity decreased for hollow-fibre membrane module in initial hours of operation, thought to be due to competitive sorption effects and concentration polarisation. NO_x and SO_x components noted to transfer from feed to CO₂ permeate stream.</p> <p>Filmtec module consisted of a thin-film composite, polyamide membrane (polypiperazine amide with the presence of free amine and carboxylate end groups, coated on a polysulfone interlayer over a polyester support) designed for nanofiltration applications. Spiral-wound module performance increased in presence of flue gas as saturated water allowed facilitated transport mechanisms to occur. Pressure drop observations also suggested only spiral-wound module suitable for PCC applications. However, permeance and selectivity were too low to be competitive with other PCC technologies (permeance 29 GPU, CO₂/N₂ selectivity 7).</p>	<p>Electrical-energy consumption of pilot plant (including feed blower and vacuum pump) ~5 GJ_e/tCO₂.</p>	<p>Scholes et al. 2015</p>
<p>Polyvinylamine pH-controlled films of polyvinylamine on polysulfone; carrier chemically bonded to polymer matrix</p> <p>Norwegian University of Science and Technology (NTNU)</p> <p>SINTEF</p>	<p>Evaluated as part of Nanoglowa project. Selectivities >500 and permeabilities approaching 2000 GPU achieved. Flat sheet module (1.5 m²) evaluated at Sines coal-fired power plant, Portugal, for 6.5 months. Module showed good resistance to NO_x, SO₂ and particulates. Produced permeate stream containing 75% CO₂. CO₂ permeance and CO₂/N₂ selectivity similar to lab determined values achieved at power plant during periods of constant power plant operation.</p> <p>18 m² hollow-fibre membrane evaluated at Norcem cement factory (17 mol% CO₂, w.b.). 70 mol% CO₂ permeate stream achieved with single stage. Membrane showed good stability to high concentrations of SO₂ and NO_x. Noted improved design for both process and module will be needed for scale-up.</p>	<p>High-level cost estimate completed based on Hysys simulation. 80% CO₂ recovery, 95% CO₂ purity, 1 million m² membrane required. Membrane unit was 40% of capital cost. Capturing 100 tCO₂/h, specific-capture cost \$46–49/tCO₂ captured. Believe costs can be reduced to \$40/tCO₂ with increase in CO₂ permeance.</p>	<p>Lockwood 2016 Sandru et al. 2013 Haag et al. 2017</p>
<p>Polyvinylamine-based fixed site carrier hollow-fibre membrane</p> <p>NTNU</p> <p>SINTEF</p>	<p>Evaluated at Tiller pilot plant (propane burner flue gas) with flue-gas CO₂ concentrations 9.5–12.4%. Semi-commercial polysulfone membrane support coated with polyvinylamine layer in-situ (8.4 m²). This follows on from flat sheet module evaluated previously.</p>		<p>He et al. 2017</p>

TECHNOLOGY COMPANY/RESEARCH INSTITUTE	DESCRIPTION	COST AND ENERGY INFORMATION	REFERENCES
	<p>CO₂ flux and permeate purity noted to increase with flue-gas CO₂ concentration. The effect of feed pressure noted to be less significant at pressures >3 bar due to smaller relative contribution of facilitated transport. Single-stage process was able to achieve 60% CO₂ purity.</p>		
<p>Facilitated transport membrane. Selective amine polymer layer on polyethersulfone membrane support Ohio State University</p>	<p>Developing CO₂ selective membrane for CO₂ capture from <1 vol% CO₂ sources. Suggested for use downstream of standard CO₂ capture plant for final polishing to increase CO₂ capture rate.</p> <p>Two-stage module process that does not require cryogenic distillation proposed.</p> <p>Currently lab-scale evaluation. Pilot-scale evaluation scheduled for 2018–2019.</p> <p>1400 GPU, 220 CO₂/N₂ selectivity (1% CO₂ feed d.b., 57 °C).</p>	<p>High-level techno-economic assessment showed CO₂-capture cost \$280/t (2011 USD)–20% increase in COE. DOE case 12 selected for cost analysis.</p> <p>31.9 tCO₂/h CO₂ captured from 1% CO₂ source. \$97m equip cost (27% membrane, 56% blowers and vacuum). COE 8.09 c/kWh for 550-MW supercritical pulverised coal plant.</p>	<p>Ho et al. 2017</p>
<p>Polymer/inorganic composite membrane Ohio State University</p>	<p>Two-stage membrane process for PCC. Membrane consists of selective amine-containing polymer cover layer, a zeolite nanoparticle layer, and a polymer support. Permeance of 820 GPU and CO₂/N₂ selectivity of 200 achieved for spiral-wound module evaluated in lab. Evaluated at NCCC on coal flue gas. Membranes showed permeance of 800 GPU, selectivity 170 after 210 h on flue-gas stream. However, after plant shut-down, selectivity dropped to 60. Loss of performance on re-start attributed to failure of sealing glue and indentations caused by spacer.</p>		<p>Salim et al. 2018 Ho et al. 2016</p>
<p>Sub-ambient temperature hollow-fibre membrane coupled with cryogenic distillation Novel poly-imide-based membrane Air Liquide</p>	<p>Membranes coupled with cryogenic distillation. CO₂/N₂ selectivity noted to increase 2–4 times ambient levels at T below –20 °C. Small amount of N₂ sweep added to permeate to increase membrane productivity with only small impact on product purity (target 60% CO₂ to feed cryogenic unit).</p> <p>Field tested at NCCC (0.3 MW_e, 6 t/d). Impurities removed before membrane module (compression, condensation, activated alumina bed). Tolerant to SO₂ and NO concentrations of 100 ppm. NO₂ concentrations above 20 ppm noted to affect membrane permeance.</p> <p>During their work, Air Liquide developed a superior high-permeance membrane, PI-2. Current development is continuing with a Department of Energy-funded project to advance the new membrane to commercial-scale, 6-inch bundles, and evaluate on flue gas at NCCC.</p>	<p>Economic assessment based on DOE case 12 (30 wt% MEA). CO₂-capture cost \$40–\$45/tCO₂ (c.f. case 12 \$55/t).</p> <p>Levelised cost of electricity anticipated to increase between 48 and 53%.</p> <p>The new high-permeance PI-2 membrane is expected to lower costs by reducing the number of membrane units required. Estimate CO₂-capture cost range \$38–42/tCO₂.</p>	<p>Hassee et al. 2014 Augustine et al. 2017</p>

Maas et al. (2016) considered the cost of a cascade membrane system for PCC, with a membrane cost of €80/m². This resulted in a levelised cost of electricity (LCOE) of 8.59 cents/kWh and a cost of CO₂ avoided of €44.7/tCO₂ (Maas et al. 2016). Van der Spek et al. (2018) considered the cost of a combined-cycle gas turbine equipped with an advanced membrane configuration with selective gas recycle compared with a plant using 30 wt% MEA, under the assumption of flexible power dispatch. Their results showed the technical performance of the MEA system to be superior to the membrane system. The main reason for this was the reduced gas-turbine efficiency resulting from the high CO₂ concentration caused by the selective recycling of CO₂ to the combustor. The full load LCOE for the membrane system was determined to be 99.7 €/MWh (c.f. 91.3 €/MWh for MEA).

2.2.1 Membrane contactors

In addition to separation devices, a membrane can also be used as a contacting device. Here the membrane is used to separate the liquid absorbent from the flue-gas stream, with the membrane providing the surface area for CO₂ mass transfer. Membrane contactors potentially provide high surface areas for mass transfer with low pressure drop, and avoid flooding and entrainment issues. One of the most notable advantages is the high interfacial area, leading to reduced equipment size. This can be particularly attractive in offshore applications, where size and weight restrictions apply. Membrane contactors have been successfully commercialised in several gas–liquid applications, such as CO₂/O₂ removal from fermentation, production of ultra-pure water and membrane distillation (Zhao et al. 2016). In PCC applications, membranes often suffer from wetting, where the liquid absorbent can migrate into the pores of the membrane, reducing the effectiveness of the contactor in practice.

Membrane contactors have been evaluated for PCC applications by Kvaerner Process systems (Falk-Pedersen, 1997), MHI (Nishikawa et al. 1995), TNO (Feron and Jansen, 1995), and the CO₂CRC (Scholes et al. 2014). Further detail of recent pilot-scale evaluation of a membrane contactor using dense polyether ether ketone (PEEK) membranes in research supported by DOE is provided in Table 18. Despite pilot-scale evaluation on flue gases, the technology has not progressed to commercial application.

Table 18 Summary of membrane-contactor processes for post-combustion CO₂ capture

TECHNOLOGY COMPANY/RESEARCH INSTITUTE	DESCRIPTION	COST AND ENERGY INFORMATION	REFERENCES
Surface modified polyether ether ketone (PEEK) membrane. Super-hydrophobic nanoporous hollow-fibre membrane Gas Technology Institute (GTI)	GTI have been developing PEEK hollow-fibre membrane contactors since 2010. Evaluated in lab (10–20 ft ²) with activated methyl-diethanolamine (aMDEA) under both absorber and desorber conditions. Performance not affected by flue-gas contaminants O ₂ (~3%), NO ₂ (66 ppm) and SO ₂ (145 ppm). Mass-transfer coefficient found to be larger than achieved with standard packed contactors. Field tests (4-inch module, 165 ft ²) achieved 90% CO ₂ capture in single stage. Membrane permeance 2000 GPU, mass-transfer coefficient 1.2 s ⁻¹ . Membrane contactor also evaluated with Hitachi’s H3-1 absorbent. Mass-transfer coefficient increased 17% compared with aMDEA. 8-inch absorber module with flash regeneration (0.5 MW _e) evaluated at National Carbon Capture Center. Achieved 85% CO ₂ capture, 98.6% purity.	Techno-economic assessment based on field tests with 4-inch module suggests cost of capture of \$47.5/t (2011 USD, Department of Energy (DOE) \$56.5/t). Increase in LCOE 57% (c.f. DOE case increase 69.6%).	Li et al. 2017

2.2.2 Hybrid and combined membrane processes

Due to the large volumes of low-pressure flue gas that require CO₂ removal from power-station flue-gas streams, creating an affordable pressure ratio to drive membrane separation is challenging (White et al. 2015). To overcome this, several researchers have proposed membrane processes. Membranes can be used in a two-step process to achieve overall CO₂ removal efficiencies of 90% for reduced vacuum requirements. Similarly, membranes can be used to improve the efficiency of a separate downstream CO₂ removal step by enriching the flue-gas CO₂ concentration. A few of these have already been discussed in detail previously, including American Air Liquide's hollow-fibre membrane process coupled with cryogenic separation (see Table 10). Further information on additional research and development is provided below.

TNO and SINTEF have evaluated membrane-assisted CO₂ liquefaction as part of the CEMCAP project, with a focus on CO₂ removal applied to the cement industry. The polymeric membranes are used to provide the bulk removal of CO₂, generating a high CO₂ concentration permeate stream. Liquefaction is then used for further purification of the permeate CO₂. This process allows CO₂ capture without the need for process steam, often not available in cement plants. Simulations suggest CO₂ concentrations >15% are required when using a single membrane stage (Bouma et al. 2017). The low-temperature separation has been evaluated at 10 t/d pilot scale treating a CO₂/N₂ gas stream (Knudsen et al. 2018, Traedal and Berstad 2018). A preliminary techno-economic assessment suggests a cost of CO₂ avoided of €84/tCO₂, which was comparable to a standard process using 30 wt% MEA (Voldsund et al. 2018).

The University of Texas and MTR have evaluated using a membrane to increase the CO₂ concentration in NGCC flue gas prior to CO₂ capture via an amine-based process (5 m PZ). Simulations showed increasing the CO₂ content in the flue gas to 12% provided the lowest total cost for the hybrid amine–membrane system (Ding et al. 2017).

Liquid Ion solutions, partnering with Penn State University and Carbon Capture Scientific, proposed a system that used a mixed matrix membrane upstream of an absorption plant. The bulk of CO₂ removal is achieved via the membrane. An air stripper is used to regenerate the liquid absorbent, with the CO₂-rich air stream supplied to combustor. This increases the CO₂ concentration in the flue gas to the mixed matrix membrane. Development of the membrane identified scale-up of the polymer systems to be challenging. Preliminary techno-economic analysis suggests process efficiency gains were insufficient to offset increased capital equipment costs (Liquid Ion Solutions 2018, Nulwala 2018).

GTI have teamed with University of South Carolina, PoroGen Corporation and Trimeric Corporation to develop a hybrid membrane process. The process will combine the GO gas-separation membrane being developed by the University of South Carolina with a solvent process using GTI's hollow-fibre membrane contactor. The GO membranes will capture the bulk of the CO₂ from the flue-gas stream (90% purity), with the PEEK hollow-fibre membrane contactor capturing additional CO₂ (99.5% purity) to meet DOE performance targets (95% purity CO₂ overall). Third-generation PEEK fibres are being developed to achieve a CO₂ permeance of 3000 GPU. GO membrane performance was enhanced by adding structural defects, shrinking flake lateral size, and adding CO₂-philic agent (PZ) between graphene layers. A CO₂ permeance >1000 GPU, CO₂/N₂ selectivity >600 (@80 °C for humidified CO₂/N₂ mixture) was achieved (Li et al. 2017).

To overcome the challenge of treating large volumes of low-pressure flue gas, MTR have proposed a two-step process, as outlined in Figure 8. A small amount of feed compression (2.4–3 bar_a), and slight vacuum (0.07–0.2 bar_a) applied to the permeate stream, are used in the first membrane stage to provide the pressure differential for CO₂ removal. Approximately 50% of the CO₂ is captured in this first stage. An air sweep using combustion air is used in the second stage for final CO₂ removal, achieving overall CO₂ capture efficiencies of 90%. The sweep stage also has the advantage of enriching the combustion air with CO₂, increasing the concentration of CO₂ in the flue-gas stream, and improving the CO₂ removal efficiency of the first membrane stage (White et al. 2015). One disadvantage of this process is the need to modify the power-station boiler to deal with the increased CO₂ content in the air. MTR have evaluated the full process, including CO₂-enriched air to the boiler, at Babcock and Wilcox’s research coal-boiler facility. Based on simulations developed as part of the work, 18% O₂ in the air to the boiler was determined to be the optimum (Hoffman et al. 2017). As the purity of the CO₂ generated is low (~60%), a downstream CPU is also required if the CO₂ is to be stored or used for enhanced oil recovery (EOR).

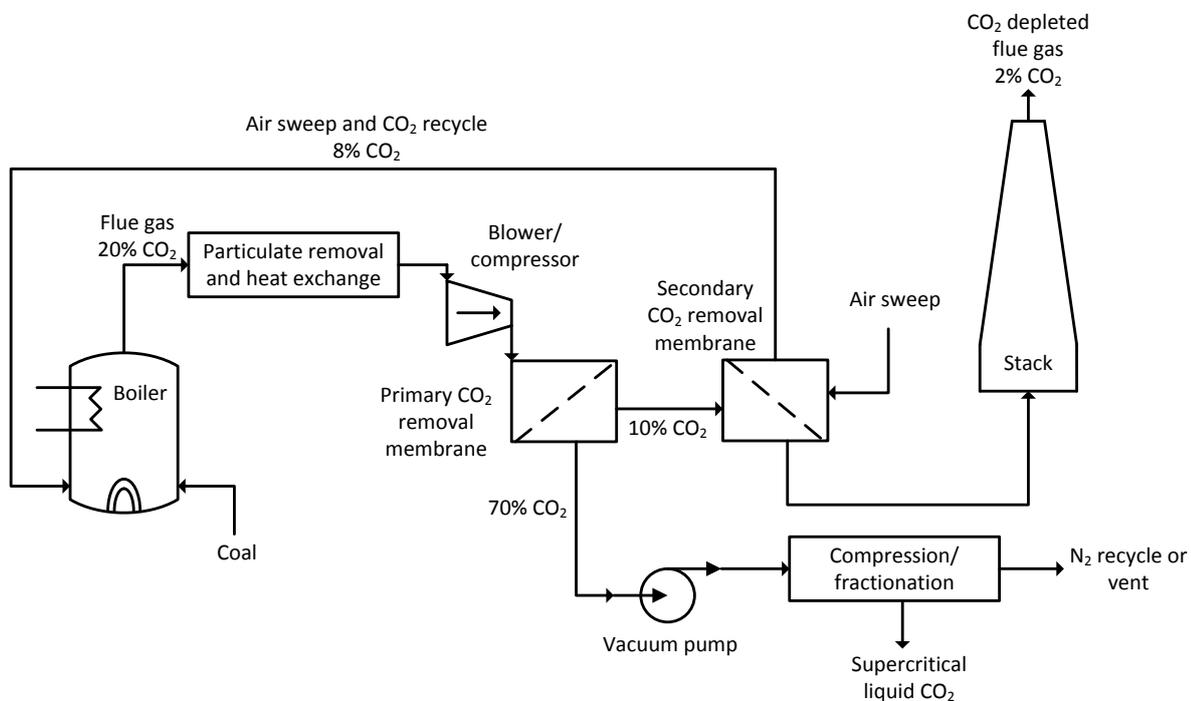


Figure 8 Flow diagram of MTR’s two-step membrane system for CO₂ capture from flue gas (White et al. 2015)

TDA Research, MTR, and the University of California–Irvine have collaborated to develop a combined membrane–sorbent hybrid system for PCC. The system integrates MTR’s membrane module with TDA’s sorbent in a two-step separation process. Successful bench-scale evaluation treating a coal flue gas was completed as part of a small business innovation research project (NETL 2018a). The project builds on previous research conducted separately by each organisation. TDA Research has achieved slipstream evaluation of their mesoporous carbon sorbent, and MTR has achieved significant pilot-scale evaluation of their membrane process. For the combined system, MTR’s membrane will operate at temperatures around 50 °C under mild vacuum conditions (~0.3 atm) and remove ~50% of the CO₂ and almost all water. TDA’s sorbent will remove the remaining CO₂ in the membrane effluent, ensuring 90% capture. Advantages include low pressure drop, and the sorbent being less affected by the low partial pressure of CO₂ in the second stage. Field tests (2–4 standard cubic feet per minute) of the hybrid system treating coal-derived

flue gas have been completed at Western Research Institute (525 h, 3200 cycles). Cost of capture for the hybrid system was estimated at \$35.5/tCO₂, 33% lower cost of capture than comparable amine-based system. The membrane–sorbent hybrid system has now been selected for evaluation at TCM (10 MW_e).

Discussion on commercialisation potential and development since previous review

Several membranes capable of selectively removing CO₂ from flue-gas mixtures have been developed. The biggest challenge is the scale of the process required when applied to power-station and large scale industrial flue gas streams, and the large, expensive and energy-consuming compression equipment required (Merkel et al. 2010). Early economic assessment of membranes using flue-gas compression for PCC suggested costs around 30% above standard amine-absorption CO₂ capture plant, with the majority of the high capital and operating costs due to the associated compressors (Hendriks 1994, Abanades et al. 2015). Using vacuum pumping on the permeate side of the membrane is expected to make membrane separations for PCC more economical, with several techno-economic assessments now suggesting CO₂ capture costs lower than comparable amine plant using 30 wt% MEA.

Generating high-purity CO₂ is limited by the efficiency of commercially available vacuum compressors. Merkel et al. (2010) have suggested that a vacuum pressure of 0.2 bar is probably the lowest vacuum pressure that can be considered practical for flue-gas CO₂ capture. Membrane system performance is restricted by the pressure ratio achievable across the membrane. As such, it is unlikely that a single-stage membrane system will be able to capture 90% of flue-gas CO₂ and produce a high-purity CO₂ permeate stream (Merkel et al. 2010). Instead, either a multi-stage membrane system, or hybrid with another CO₂ capture process, will be required to achieve high CO₂ recovery and purity. As part of the recent DOE project, Worley Parsons completed a techno-economic assessment of MTR's membrane process. With the exception of the membrane modules, the balance of process equipment selected were commercial equipment available today in the required sizes (Merkel et al. 2016).

Significant advances in membrane technology for PCC have been achieved, particularly through the large pilot-scale evaluation on real flue gases achieved by MTR. MTR have evaluated 0.2-m diameter, 1-m long, membrane modules on real flue-gas streams. They have demonstrated that membranes up to 1 m wide can be manufactured on commercial equipment and meet specifications for operating on real flue-gas streams. A membrane of this size was able to capture CO₂ at a rate of 1 t/d. A typical 600-MW coal-fired power plant will emit roughly 11,000 t/d CO₂, and would thus require tens of thousands of such modules for full-scale capture (White et al. 2017). This is similar to the scale of current, large reverse-osmosis plants. This would also require hundreds of thousands to millions of square metres of membrane per full-scale installation (White et al. 2015). Scale-up in other applications has been achieved via stacking of membrane modules. Currently there is little experience integrating several membrane modules in flue gas streams with vacuum.

While detailed cost and energy studies have been completed for membrane-based PCC, van der Spek (2018) highlights that there is still limited detailed techno-economic performance data for real systems in the public domain. White et al. (2017) note that a key assumption in most membrane cost studies is the long-term stability of the membrane under flue-gas conditions spanning multiple years. While increasing, experimental evaluation of membranes under PCC conditions has not yet reached this level. The base-case membrane skid cost used in economic studies has typically been

in the range \$50–100/m². Merkel et al. (2010) note that this cost is currently lower than commercial gas-separation membrane skids (\$500–750/m²). However, industrial gas-separation systems operate at high pressure with flammable gases, increasing the cost of membrane skid components. They suggest a more relevant comparison is to large, commercial reverse-osmosis systems. These plants are of similar scale to what would be required for membrane-based PCC, and can be made from cheaper components (membrane skid cost <\$50/m²).

In the previous IEAGHG review it was noted that several tests of membranes at reasonable scale using flue gas had already been achieved. Membranes are already used at larger scale for similar separation of CO₂ from CH₄. Thus, the TRL was assessed as being at 6, with potential for rapid wide scale deployment. Most of the development of PCC membranes has been in polymeric membranes. Abanades et al. (2015) evaluated inorganic membranes for CO₂ separation to be at TRL 2–3.

The evaluation of membranes for PCC application is still receiving significant attention. While the membranes themselves have been evaluated for separation and stability in flue-gas streams, only recently has the full automated system been evaluated at pilot scale. While the membrane materials themselves are at a TRL of 6, some of the process concepts incorporating membranes are at a lower level of development. For example, the MTR process incorporating flue-gas recycle has now been demonstrated on a coal research boiler. This suggests that while the membranes could achieve a TRL of 7 after MTR's planned evaluation at TCM, the TRL of the full process will still be lower than this.

Membrane-contactor processes do not appear to have been covered in the previous review. Membrane contactors have been commercialised in other industries and different applications. As noted above, challenges still remain when applied to PCC with liquid absorbents. GTI, however, have achieved small pilot-scale evaluation on flue gas streams, suggesting the technology has advanced to a TRL of 5–6. While scale-up of membrane modules will face similar challenges to other PCC membrane technologies, the lack of need for vacuum equipment suggests some scale-up challenges could be avoided for these systems. Long-term evaluation proving membrane durability under process conditions, however, still needs to be achieved.

2.3 Adsorbents

Solid sorbents are potentially a lower-energy alternative to liquid absorbents. Here the target gas species adsorbs onto the solid surface. Once the solid is saturated, the adsorbent can be regenerated via temperature, pressure (also vacuum) or electrical swings. Binding of the target gas molecule to the solid surface can be via physical or chemical sorption.

While physisorbents tend to have lower adsorption enthalpies than chemisorbents, they also typically exhibit lower CO₂ loadings and selectivities (Lockwood 2016). Chemisorption can be achieved by introducing amine groups or other chemically active surface modifications that form a bond with CO₂. This can make the sorbent highly selective for CO₂, allowing the production of high-purity CO₂, but regeneration often requires energy-intensive temperature swing processes. In physisorbent processes, as bonding of the target gas to the sorbent material is generally weaker (compared with chemisorbents) regeneration via pressure swing can be rapid. In pressure-swing adsorption (PSA, or VPSA if vacuum is used) the driving force for separation is supplied by a change

in pressure between the adsorption and desorption steps. However, the CO₂ purity produced from a single stage can be low. To achieve CO₂ purities >95%, two or more stages are typically used.

For chemisorption, where the bonding of CO₂ to the sorbent material can be stronger, regeneration may require the more energy-intensive temperature swing. In temperature swing adsorption (TSA), the driving force is supplied via temperature change (Berger et al. 2017). As it can take substantial time to increase the temperature of the sorbent material to regeneration temperatures, the cycle time for TSA processes can be longer. For solid-sorbent systems to be cost effective, short cycle times are critical. Abanades et al. (2015) show that if the regeneration cycle time can be reduced from 1 h to 1 s, the volume of sorbent material required to capture CO₂ from a full-scale power plant would decrease from 22,900 m³ to only 6.35 m³. This would obviously have a significant impact on the capital cost of the process. However, at full-scale rapid swing processes will require the opening and closing of extremely large valves. There will be a mechanical limit to how quickly these valves can open and close whilst maintaining reliability.

In electrical swing absorption (ESA), an electric current is applied to the sorbent material. This heats the sorbent via the direct Joule effect, providing the energy for regeneration. ESA is considered fundamentally limited from a thermodynamic perspective, and as such is considered unsuitable for treating large volumes of gas (Lockwood 2016). ESA was evaluated by the Polytechnic University of Milan and SINTEF as part of the EU MATESA project. They simulated ESA for a NGCC. Their preliminary simulation results suggest an efficiency penalty double that of a MEA-based process (Bonalmi et al. 2017). Similar results were achieved with a combined ESA/TSA process (Lillia et al. 2017).

An advantage of solid-sorbent systems is that there is no need to heat significant volumes of water, as is the case with liquid-absorbent systems, though there will still be some sensible heating and cooling requirement of the solid materials. Sorbents will need to be tolerant of water vapour present in flue gas streams. Sorbent systems typically have faster kinetics than aqueous absorbents, and cyclic CO₂ capacities can be higher on a weight basis. Solid sorbents are also less volatile and can be suited to the production of high-pressure CO₂. Solids handling, and achieving suitable heat transfer for regeneration, are more challenging. In addition, moisture management for solid-sorbent systems can be difficult and bed particle voidage can decrease product purity (Lockwood 2016, Berger et al. 2017). Solid adsorbents for CO₂ capture have already found commercial application in the gas-processing industry. They are particularly useful for final polishing stages, removing the last few per cent of CO₂ from the gas mixture, making them particularly applicable to air separation as long as the flow rate of captured CO₂ remains small.

Commonly used sorbent materials include activated carbons, zeolites, carbonates, supported amines and MOFs. Activated carbons are attractive, as they are low-cost sorbents with high surface areas. They are fairly tolerant to moisture, but can lose a small amount of capacity on exposure to moisture (Berger et al. 2017). Zeolites are a group of crystalline, microporous aluminosilicates with large surface areas (Lockwood 2016). Sufficiently narrow pores (~3.6 Angstroms) can enhance the selectivity of zeolites through molecular sieving. Zeolites, however, are highly hydrophilic and can be poisoned by exposure to even small amounts of moisture. A separate guard layer of sorbent, or other flue-gas drying mechanism, may be required upstream to protect the CO₂-removing zeolite sorbent (Lockwood 2016, Berger et al. 2017, Abanades et al. 2015). Solid metal carbonates (Na₂CO₃, K₂CO₃) are another low-cost solid sorbent with high capacities and high water tolerance.

They will react with CO₂ and water to form a bicarbonate, with regeneration at high temperature, which can be energy intensive (Lockwood 2016). Hitachi have evaluated a CeO₂-based sorbent for CO₂ capture that shows similar adsorption capacities under both dry and humid conditions (Yoshikawa et al. 2017). RTI are evaluating hybrid-phosphorus dendrimer adsorbents as part of a DOE-funded project. These sorbents have exhibited good stability over 250 cycles (Soukri et al. 2017).

Solid sorbents (typically mesoporous silica) can be impregnated with amines. These supported-amine sorbents show enhanced CO₂ selectivity and good working capacities under PCC conditions. The amine polymer polyethyleneimine (PEI) is widely used for this purpose. Maintaining good adhesion between the two components under operating conditions can be challenging (Lockwood 2016). Monash University have evaluated PEI composite powders fabricated into pellets. While the CO₂ capacity of the pellets was slightly lower than the powder precursor, they also exhibited high water tolerance (Knowles and Chaffee 2017). Aspen Aerogels, in collaboration with the University of Akron, have evaluated amine-functionalised aerogel pellets for CO₂ capture. Sorbents were evaluated in a bench-scale, fluidised-bed reactor and showed high CO₂ capture capacities. Preliminary techno-economic assessment, however, suggested a higher cost of capture compared with 30 wt% MEA (Begag 2017).

MOFs are compounds consisting of metal ions (clusters) coordinated to organic ligands. These synthetic, solid sorbents can exhibit very large surface areas and porosities. Unfortunately, the high CO₂ capacities displayed by early materials are usually only valid for high CO₂ partial pressures. Under PCC conditions, capacities tend to be comparable to zeolites (Lockwood 2016). The synthesis of MOFs is currently costly and challenging to scale-up. As such, few MOF materials are available in commercial quantities. A significant amount of research and development has been conducted into solid sorbents for PCC applications. Heriot-Watt University have evaluated MIL-53 and HKUST-1 MOFs under PCC conditions. Ethanolamine was used as an additive to promote CO₂ sorption; however, the sorbents were found to be ineffective under PCC conditions (Ba-Shammakh et al. 2017). Park et al. (2017) identified several MOFs that can achieve >10 mol/kg swing capacities at sub ambient conditions. RTI is evaluating a hybrid MOF as part of a DOE-funded project, where MOF nanocrystals are formed within the pores of the solid sorbent (Soukri et al. 2017). Lawrence Berkeley National Laboratory is developing MOFs coated with alkyl amines to improve working capacities (Neaton et al. 2018). The sorbent shows stability to humid conditions and oxidation at high temperature, and is now being evaluated for inclusion into Inventys rotating packed-bed system.

CO₂ capture with solid sorbents faces several challenges. These include material handling, heat transfer, pressure gradients, flow distribution, operability, system size, moisture management, energy consumption, and mechanical and chemical durability (Berger et al. 2017). Thus, operational experience on real flue gas streams is critical. Table 19 provides a summary of research undertaken evaluating various solid sorbents for CO₂ removal under PCC conditions, with a particular focus on those that have been evaluated at pilot scale, or where techno-economic assessments have been completed. A flow diagram of the RTI process, which utilises fluidised bed reactors, is provided in Figure 9.

Table 19 Summary of solid sorbent processes for post-combustion CO₂ capture

TECHNOLOGY COMPANY/RESEARCH INSTITUTE	DESCRIPTION	COST AND ENERGY INFORMATION	REFERENCES
Activated and other carbons			
VeloxoTherm Inventys Thermal Technologies	<p>Uses rotating packed bed of structured, solid sorbent (sorbent from commercial suppliers, fabricated into structured adsorbent beds at Inventys). Stages include CO₂ adsorption, bed regeneration using low-pressure (LP) steam temperature swing adsorption (TSA), conditioning (hot air to remove remaining moisture), and air cooling. Design based on commercial rotary air pre-heaters should assist scale-up and power plant compatibility. Scale already comparable to that required for PCC. Seals used in current pre-heaters not sufficient for VeloxoTherm. Instead use proprietary seal designs.</p> <p>Evaluated at 1 t/d pilot scale.</p> <p>Received Department of Energy (DOE) funding to evaluate technology on 10-MW_e slipstream. 15-m diameter wheel for 10-MW_e pilot (30-m diameter wheel for commercial design). Project did not move to phase 2 due to budgetary estimate being above what project partners were willing to commit. Determined that additional work required on sorbent selection (need to increase bed density to achieve DOE target). Other risks identified with scale-up included leakage of sealing valves under vacuum conditions.</p> <p>Inventys recently received funding to assist development of 30 t/d pilot plant at Husky Energy's Pike Peak South Lloyd thermal project.</p>	<p>Completed techno-economic assessment for 550-MW plant (DOE case 12). Required four 30-m rotating absorbent machines. 2 stages per wheel, 0.15–0.3 rpm.</p> <p>Net plant efficiency 30.7% (higher heating value), first-year cost of electricity (COE) \$117.63, cost of CO₂ capture \$39.7/t (assuming 100% capacity factor).</p>	<p>https://vimeo.com/145198917</p> <p>Carbon Capture Journal 2011</p> <p>Greeson 2016</p> <p>Inventys 2018</p>
Mesoporous carbon with grafted surface functional groups TDA Research	<p>Initially developed for pre-combustion capture applications, TDA have now evaluated the sorbent for post-combustion capture. While still bonding strongly, CO₂ does not form a true covalent bond with surface sites, thus regeneration can be carried out with low heat input (4.9 kCal/molCO₂). Adsorbent also shown to be tolerant of flue-gas contaminants (SO₂, NO_x). Lab-scale apparatus able to achieve 98% CO₂ capture with 90–95% CO₂ purity. Slipstream (4 standard cubic feet per minute) evaluation completed at Gas Technology Institute (GTI)'s combustion facility. 4-bed vacuum-swing adsorption system achieved 95% CO₂ capture and 90% CO₂ purity.</p> <p>Sorbent production scaled up with several m³ sorbent produced.</p>	<p>Bench-scale tests suggest potential capture cost of 47 US\$/t CO₂ (\$66/tCO₂ for amine scrubber) and a COE of 122 US\$/MWh (147.3 US\$/MWh for amine scrubber).</p>	<p>Alptekin et al. 2015</p> <p>Jayaraman et al. 2018</p>
Activated-carbon microbeads SRI International	<p>Continuous, falling micro-bead sorbent reactor geometry integrates absorber and stripper into single column.</p> <p>Bench-scale tests on simulated flue gas achieved 90% CO₂ capture producing 98% pure CO₂. Operation was stable over 1000 cycles.</p>	<p>Preliminary techno-economic assessment suggests LCOE 8.77 cents/kWh, 37% increase compared with plant with no capture (c.f. 80% increase for MEA).</p>	<p>Krishnan et al. 2014</p> <p>Hornbostel 2015</p> <p>SRI 2016</p>

TECHNOLOGY COMPANY/RESEARCH INSTITUTE	DESCRIPTION	COST AND ENERGY INFORMATION	REFERENCES
	<p>135h (7000 cycles) achieved on flue-gas slipstream from coal-fired boiler (4.5% CO₂) achieving 85–95% CO₂ capture.</p> <p>Evaluated at NCCC (0.5 MW_e). CO₂ capture of 67% and CO₂ product purity 93% achieved. Increased capture could be achieved by increasing height of absorber. Steam demand higher than anticipated due to heat losses.</p>	Updated economic assessment suggests CO ₂ -capture cost of \$45/tCO ₂ (c.f. \$66.17 for MEA), and 45.9% increase in COE.	
Carbon-fibre monolith CSIRO	Carbon-fibre monolith evaluated on flue gas slipstream. Over 200 absorption/desorption cycles completed. Desorption via heating and vacuum pumping. 98% CO ₂ capture achieved (with and without pre-treatment) with 97% purity when CO ₂ flushing also used for regeneration. Sorbent showed good stability in presence of flue-gas impurities.	Preliminary economic analysis completed for 350-MW coal-fired power station. Cost of CO ₂ avoided \$77 AU/tCO ₂ .	Thiruvengkatachari et al. 2015
Zeolites			
TPECO MHI	Pilot plants treating 1000 Nm ³ /h flue-gas slipstream. Upstream dehumidification step followed by 2-stage CO ₂ removal to achieve 90% CO ₂ capture at 99% purity. Pressure (vacuum) and thermal swing regeneration. Adsorbent remained effective after 4,000 h of operation.	2.02 GJ _e /t CO ₂ work energy consumption. Expectation could reduce to 3 GJ/t CO ₂ thermal equivalent with more efficient vacuum pumps. However, need for thermal regeneration increased cycle times and eliminated much of the advantage of PSA.	Lockwood 2016 Ishibashi et al. 1996
Zeolite crystals coated onto Catacel cores WR Grace and Co. University of South Carolina Battelle Memorial Institute Catacel corporation	Developed rapid pressure-swing adsorption (PSA) process to lower cycle times. Structured sorbent lowers pressure drop and attrition issues. Laboratory-scale evaluation of 4-bed PSA process.	Preliminary techno-economic assessment suggests cost of CO ₂ avoided \$39.7/tCO ₂ (c.f. \$54.4/tCO ₂ for DOE case 10). 52.7% increase in cost of electricity.	Ritter 2015
13X APG and activated-carbon beads East China University of Science and Technology	Evaluated at pilot-scale at coal-fired power plant in China (15–17% CO ₂). Pilot plant consisted of dehumidifying unit and two successive vacuum pressure-swing adsorption (VPSA) units. 13X APG zeolite in first stage for bulk CO ₂ capture at 70–80% purity, activated-carbon beads in second stage to achieve 95% purity CO ₂ . 90% capture with 95% purity CO ₂ achieved via 2-step method.	Power consumption of 2.44 GJ _e /tCO ₂ (theoretical power consumption calculated to be 0.75 GJ _e /tCO ₂). Half of energy consumption associated with first-stage vacuum pump.	Wang et al. 2013 Lockwood 2016
5A East China University of Science and Technology	Evaluated at pilot scale at coal-fired power plant in China. Flue gas 15% CO ₂ after dehydration. 3-bed VPSA unit. 79% CO ₂ capture producing 85% CO ₂ .	Power consumption 2.37 GJ _e /tCO ₂ .	Liu et al. 2012
13X Korean institute of Energy research	2-stage vacuum (VPSA) unit preceded by pre-scrubber and drier. Treated flue gas from boiler (10.5% CO ₂) CO ₂ concentrated to 40–60% in first stage, 99% CO ₂ purity achieved in second stage.	2.3–2.8 GJ _e /tCO ₂	Cho et al. 2004 Abanades et al. 2015

TECHNOLOGY COMPANY/RESEARCH INSTITUTE	DESCRIPTION	COST AND ENERGY INFORMATION	REFERENCES
13X National University of Singapore	Evaluated in synthetic dry flue-gas stream (15% CO ₂ , 85% N ₂), regeneration via VPSA. Single bed able to achieve 86% CO ₂ capture with 96% CO ₂ purity. Alternate four step cycle able to achieve 90% capture with 95% CO ₂ purity.	1.7 GJ _e /tCO ₂	Abanades et al. 2015 Krishnamurthy et al. 2014
Carbonates			
Proprietary adsorbent based on K ₂ CO ₃ Korean Electric Power Company Korean Institute of Energy Research	Sorbent produced by commercial supplier. Sorbent consists of 35 wt% active material and 65 wt% support for mechanical strength. Evaluated on a 10-MW _e pilot plant treating coal flue-gas slipstream. Pilot-plant carbonator is a transport-type reactor (40–80 °C), with a bubbling fluidised bed reactor for the regenerator (140–200 °C). Cooling tubes are used in the carbonator to maintain reactor temperature. 1000 h continuous operation achieved with 80% CO ₂ capture and 95% CO ₂ purity.		Lockwood 2016 Park et al. 2014
CACHYS Alkali carbonate hybrid solid sorbent University of North Dakota	Evaluated at bench scale treating slipstream of steam plant flue gas. Operational challenges typically resulted in CO ₂ capture rates below 90%. Sorbent attrition also identified as an issue.	Initial techno-economic analysis suggests CO ₂ -capture cost of \$36.19/ton (DOE case 12 \$38.5/ton), corresponding to a 40% increase in COE.	Benson et al. 2015
Supported amines			
Amine supported on ion-exchange resin ADA-ES	Evaluated at 1-MW _e pilot plant treating flue-gas slipstream. Pilot-plant performance lower than anticipated primarily due to sorbent working capacity 20% lower than expected. 90% capture achieved at low flue-gas flow rates. Affected by moisture uptake, CO ₂ purity 80–90%. Regeneration via TSA. Sorbent stable over pilot-plant campaign.	Economic evaluation determined bubbling fluidised beds should be used for absorber and desorber. Techno-economic assessment showed similar levelised COE to MEA-based process (143.6 \$/MWh c.f. 147.7 \$/MWh, DOE case 10). Results were higher when pilot-plant results used for economic assessment.	Krutka et al. 2013 ADA 2016
Sorbent-polymer composite (SPC) WL Gore Electric Power Research Institute	Powdered solid sorbent incorporated into hydrophobic polymer substrate. Hydrophobicity allows direct steam heating and water cooling, minimising cycle time and increasing cyclic capacity.	Laboratory-scale analysis suggests that the SPC system will be 20 times smaller than conventional solid-sorbent systems.	Berger et al. 2017
Amine-coated porous material Kawasaki Heavy Industries (KHI) Research Institute of Innovation Technology for the Earth (Japan) (RITE)	Fixed-bed CO ₂ capture technology developed for conditioning enclosed atmospheres (such as aircraft) is being applied to industrial CO ₂ capture. Waste heat (60 °C) can be used for regeneration. A 10 t/d CO ₂ pilot has been tested. 5 t/d moving bed facility also being evaluated. New amine-impregnated solid sorbent developed by RITE to be evaluated in KHI moving bed pilot plant.	1.6 GJ _e /t CO ₂ of electrical power required to drive the process (where waste heat can be used for regeneration) for cement plant. 1.3 GJ _e /tCO ₂ for gas engine flue gas.	Okamura 2014 Lockwood 2016 Numaguchi et al. 2017

TECHNOLOGY COMPANY/RESEARCH INSTITUTE	DESCRIPTION	COST AND ENERGY INFORMATION	REFERENCES
<p>Sorbent material based on CO₂-philic polyamine (polyethyleneimine, PEI) loaded on high surface are support material (silica)</p> <p>RTI International</p>	<p>Sorbent material first developed at Pennsylvania State University (heat of absorption ~66 kJ/molCO₂). Used in a thermal swing process with dual-fluidised, moving bed reactors.</p> <p>Development has lowered cost of sorbent, improved resilience (to allow fluidisation), and improved thermal stability. Achieved CO₂ capacities of 11.8 wt% CO₂ in fluidisable form and completed parametric and long-term evaluation.</p> <p>Parametric and long-term (100 h) evaluation completed in synthetic flue gas at bench scale (150 kgCO₂/d), and field test treating gas stream at cement plant (150 h). SO₂ noted to lower sorbent capacity, hence upstream caustic scrubber required.</p>	<p>Impregnation method scaled up to 300 kg scale by commercial sorbent manufacturing partner.</p> <p>Aspen analysis used to complete preliminary techno-economic assessment. Decrease in PC plant efficiency of 7.5% points (c.f. 11.9% point for DOE case 10). Capture cost \$39.7 \$/tCO₂, 58% increase in COE (c.f. 86% for DOE case 10).</p> <p>Capture cost revised to \$43.3/tCO₂ based on lessons learned.</p> <p>Economic analysis for gas-fired facility suggest COE \$81.2/MWh (c.f. \$85/MWh for amine process).</p> <p>Economic evaluation completed for cement plant suggests cost of CO₂ avoided between 38.6–45.8 €/tCO₂ (depending on level of waste heat integration used).</p>	<p>Nelson et al. 2017</p>
<p>Multi-stage fluidised-bed process with low (PEI sorbent), mid (MgO sorbent) and high-temperature (Li₄SiO₄ sorbent) stages</p> <p>Korea Research Institute of Chemical Technology</p>	<p>Each stage has absorber and regenerator. Uses intra and inter-stage heat exchangers. Evaluated on 60 Nm³/h bench-scale unit (synthetic flue gas). 4.65 GJ/t regeneration energy achieved for single low-temperature stage. Poor performance on single-stage unit due to poor performance intra-stage of heat exchange.</p>	<p>Economic assessment based on laboratory data suggests regeneration energy of 2.37 GJ/tCO₂. Total utility cost of \$39.1/tCO₂ (\$24.5/tCO₂ with steam turbine).</p>	<p>Park et al. 2017</p>
<p>Metal organic frameworks (MOF)</p>			
<p>Polymer/MOF sorbent composite hollow fibres</p> <p>Georgia Institute of Technology</p> <p>Inmondo Tech</p>	<p>Microfluidic technique used to synthesise MOF particles inside hollow, polymer fibres.</p> <p>DOE-funded project to evaluate 10 mol/kg sorbent swing capacity novel polymer/MOF sorbent composite hollow fibres in a rapidly cycled PSA (RCPSA) process. Sub-ambient RCPSA process integrates flue-gas conditioning with compact PSA system. Efficiency of PSA cycle enhanced by installing phase-change material in pores of the hollow-fibre sorbents to isothermally melt upon release of sorption enthalpy and conversely freeze upon CO₂ desorption, removing steam/cooling-water requirement. Currently bench-scale evaluation, with several MOFs identified that are</p>	<p>Initial high-level process analysis based on 10 mol/kg swing suggested a CO₂-capture cost of \$21/t, requiring 36,000 8-inch modules. This was recently updated to anticipated costs in the range \$35-45/tonne CO₂</p>	<p>Lively et al. 2017</p> <p>Pimentel et al. 2017</p> <p>Lively et al. 2009</p> <p>NETL 2018h</p> <p>Lively 2015</p> <p>Walton et al. 2018</p>

TECHNOLOGY COMPANY/RESEARCH INSTITUTE	DESCRIPTION	COST AND ENERGY INFORMATION	REFERENCES
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able to meet the 10 mol/kg swing capacity at sub-ambient conditions.

Earlier work considered rapid thermal swing process.
Current project progressing RCPSA process.

Other

Alkalisied alumina adsorbent
TDA Research

Low-cost, dry solid sorbent with long cycle life. CO₂ adsorbs to alkali surface sites. Heat of desorption 3–10 kcal/mole CO₂ (condition dependant). Stable to NO_x and water, slow loss of CO₂ capacity with CO₂ capture, but able to be reconditioned. Regeneration with low pressure (~1 atm) superheated steam, not requiring temperature or pressure swing. Fixed-bed process. 100 h field test completed at Western Research Institute’s combustion test facility.

To be evaluated at 0.5 MW_e (10 t/d) scale at NCCC. Commercial supplier used to manufacture adsorbent. 90% CO₂ capture achieved in continuous bench-scale rig with commercially produced sorbent.

Aspen simulation completed for capture applied to subcritical power station. Capture cost \$45/tCO₂ (c.f. \$59/tCO₂ for amine). 4.77 cents/kWh increase in LCOE (c.f. 6.92 cents/kWh for amines). Estimated to improve to \$36/tCO₂ (\$46.2/tCO₂ avoided) when fully developed.

Elliot et al. 2013
Elliot et al. 2017

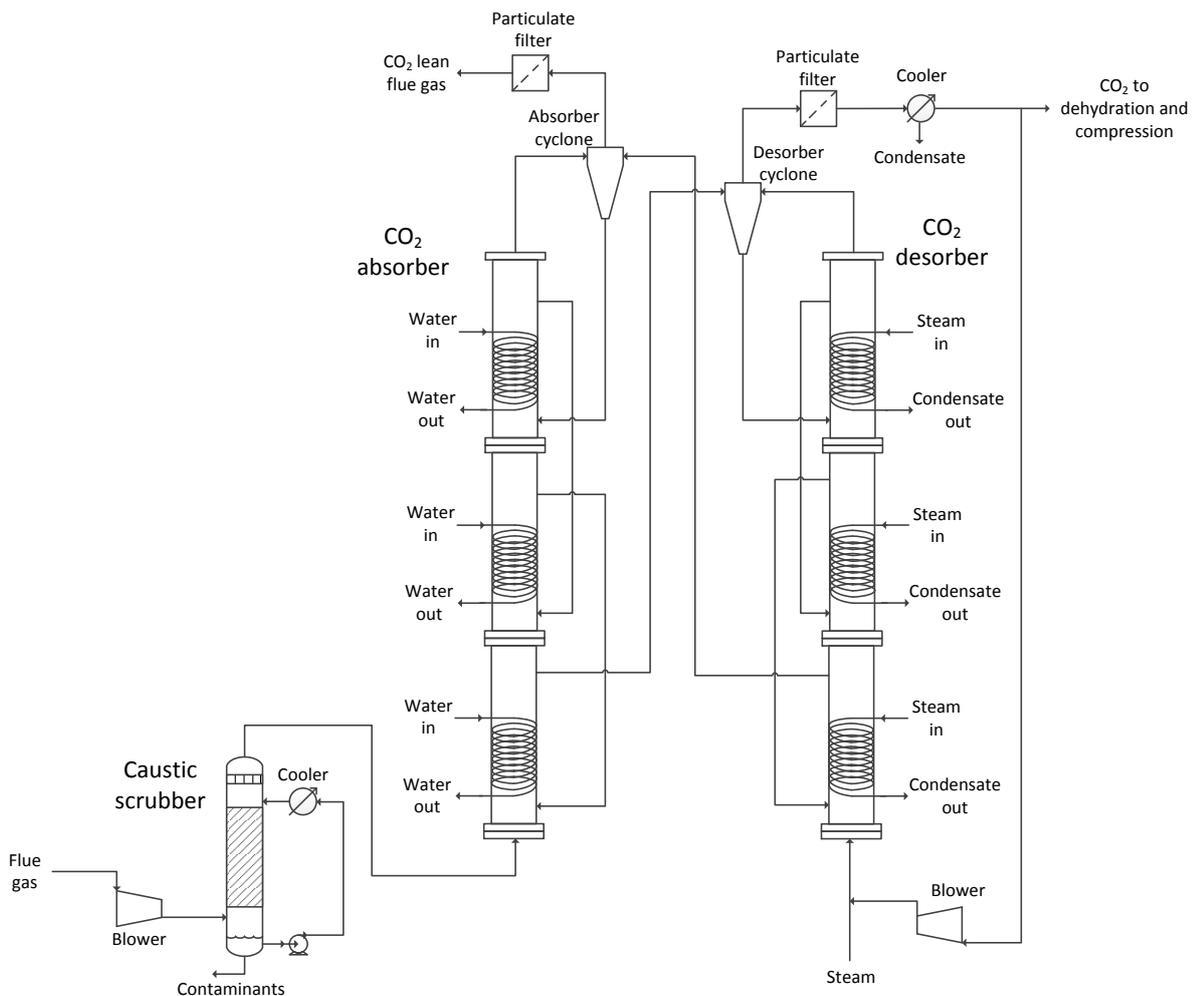


Figure 9 Flow diagram of RTI’s solid sorbent CO₂ capture process (Nelson et al. 2017)

Discussion on commercialisation potential and development since previous review

For physisorbents, PSA/VPSA regeneration is typically used. As these sorbents tend to bind CO₂ less strongly, selectivity and loading capacity can be low, leading to low CO₂ purities and capture rates. VPSA processes are more favourable at higher concentrations of CO₂, with 10% suggested as the minimum level needed (Lockwood 2016). VPSA pilots have tended to use a second capture stage to enhance capture rate and purity. The vacuum pump is one of the largest contributors to the overall energy requirement of VPSA, with CO₂ purity linked to the vacuum pressure used. The pressures required to achieve 95% purity CO₂ in a single stage are currently outside the practical capabilities of large-scale vacuum pumps (Lockwood 2016). A more economic approach may be to use a CO₂ purification unit downstream of the separation step. In the previous review, while the principals of VPSA were well proven, applications for CO₂ capture had only been demonstrated at very small scale. In addition, a sorbent with the desired properties for economic commercial operation was yet to be evaluated. As such, VPSA processes were assessed as being at a TRL of 3. Several PSA pilot plants have now been evaluated on coal flue gases, particularly with zeolites. The current electrical-energy requirements of these processes (typical >2.3 GJ_e/tCO₂) are significantly higher than the theoretical power consumption, with the main power requirement being for the vacuum pumps. Results are not as yet superior to liquid-absorbent-based PCC processes.

TSA regeneration is less developed, but is an active area of research due to the ability to produce high-purity and high-pressure CO₂ in a single step (Lockwood 2016). However, heating a large mass of sorbent can require long time scales, limiting their effectiveness and increasing costs. For TSA applications in particular, the use of fluidised beds has been suggested. While providing greater contact between the gas and solid phase, handling large quantities of moving solids is complex, requiring careful optimisation and process control (Lockwood 2016). With fluidised-bed processes, more stringent limitations are placed on the size and density of the sorbent particles to ensure efficient fluidisation and mechanical strength to avoid attrition and prevent excessive material loss (Lockwood 2016). In the previous review it was noted that while the principles of TSA processes are well understood, formulation of an application that would be competitive in energy consumption, practicality and cost, was yet to be developed. Again, a sorbent with adequate properties and performance had not as yet been identified. As such, the TRL of TSA processes was assessed as being at a TRL of 1. A few pilots operating on flue-gas streams have now been realised. Of particular interest is the rotating packed bed containing structured solid sorbents being developed by Inventys. The parallels of this process with current commercially available air-preheaters removes several of the risks associated with technology scale-up. However, a large-scale pilot is still yet to be achieved. Challenges with sealing under vacuum-regeneration conditions, and challenges with capillary pore condensation in sorbent material have been identified.

The developments since the previous review suggest that both PSA and TSA processes have matured to a TRL of 6. With TDA Research being selected for evaluation of their sorbent (combined with MTR's membrane) at TCM, and the 10-MW_e pilot being operated in Korea, these technologies may shortly progress to a TRL of 7. Long-term (>1000 h) evaluation on real flue-gas streams, however, is still lacking for this technology.

Solid-absorbent processes are already used in other industries, such as purification of natural gas. Assuming standard production methods can be used for new adsorbents developed, the

development in other industries suggests that scale-up of this technology should also be straightforward.

2.4 Cooling and liquefaction

Low-temperature separation involves cooling the flue-gas stream to the point where the CO₂ forms a liquid or solid that can be separated. Potential advantages of low-temperature CO₂ capture compared with baseline solvent-based capture include: no chemicals needed (and hence no make-up requirements or emissions), and no requirement for steam extraction (avoids need to modify power-station steam cycle) (Berstad et al. 2013). The energy required for the CO₂ capture process depends strongly on the flue-gas CO₂ concentration and the CO₂ capture efficacy. The standalone carbon-capture ratio for CO₂ liquefaction follows CO₂/N₂ vapour–liquid equilibrium data and depends strongly on the pressure and temperature of the phase separation. Typical conditions for liquefaction are 20–40 bar and temperatures down to around –55 °C (Bouma et al. 2017). Berstad et al. (2013) reviewed low-temperature CO₂ separation processes for combustion flue gases. Flue-gas CO₂ concentration was noted to have a large effect on the separation and compression work required, and also the achievable CO₂ capture efficiency for separation of liquid CO₂. For typical combustion flue gases with CO₂ concentrations in the range 4–15 vol%, CO₂ capture efficiencies below 50% are expected. However, if the CO₂ is frozen, then vapour–liquid equilibria no longer apply, and 100% capture of the CO₂ is theoretically possible. These processes are sometimes referred to as cryogenic separation. However, cryogenic temperatures have been defined as those below –153 °C, which are not always reached for the CO₂ capture processes considered here (Berstad et al. 2013).

Air Liquide is developing a hybrid-membrane, liquefaction process. Here a membrane is used to concentrate the CO₂ stream sent to the liquefaction plant. An overview of this process has already been provided in the Membrane section of this report. Table 20 provides a summary of other research ongoing in this space.

Table 20 Cooling and liquefaction processes for post-combustion CO₂ capture

TECHNOLOGY COMPANY/RESEARCH INSTITUTE	DESCRIPTION	COST AND ENERGY INFORMATION	REFERENCES
Frosting and defrosting of CO ₂ at atmospheric P in a low-temperature evaporator Ecoles de Mines Alstom	Flue gas is initially cooled to remove water. CO ₂ frosting is then performed via a cascade of up to six refrigerants. The triple point of CO ₂ is at 520 kPa, –56.6°C. At a pressure lower than the triple-point pressure, CO ₂ goes directly from the gas phase to the solid phase. The frosting–defrosting process is performed alternatively in two evaporators, one frosting while the other defrosts, with the recovery of liquid CO ₂ . The design of the frosting/defrosting on the heat exchanger surface permits the recovery of fusion heat via the refrigerant blend when CO ₂ changes from solid to liquid. However, build-up of solid CO ₂ on heat-transfer surface reduces heat-transfer and increases pressure drop. Also inefficiency with cycling temperature of heat exchangers.	Preliminary economic assessment with 90% capture suggests total energy consumption between 0.65 and 1.25 GJ/tCO ₂ depending on the cooling system efficiency (coefficient of performance values of 80 or 50%). This corresponds to an energy penalty between 11 and 22% for a 660-MW coal-fired power plant. Economic analysis completed by Schach et al. (2011) showed better performance but overall higher cost of the anti-sublimation CO ₂ capture system compared with a MEA-based process.	Clodic et al. 2005 Clodic and Younes 2003 Schach et al. 2011 Lockwood 2016

TECHNOLOGY COMPANY/RESEARCH INSTITUTE	DESCRIPTION	COST AND ENERGY INFORMATION	REFERENCES
Cryogenic CO ₂ capture (CCC) process Brigham Young University Sustainable Energy Solutions	<p>Two processes being developed: compressed flue gas (CCC-CFG), and external cooling loop (CCC-ECL). Both processes make use of recuperative heat exchange and are able to remove additional flue-gas components.</p> <p>In CFG, flue gas is dried and cooled, modestly compressed (~6 bar), then cooled further to a temperature slightly above CO₂ de-sublimation temperature. The gas is then expanded to precipitate CO₂. This process has been scaled up to 0.25 tCO₂/d and evaluated on flue-gas slipstreams from a variety of sources.</p> <p>In ECL, flue gas is cooled by an external refrigerant loop. Flue gas is initially cooled to remove water. Further cooling is achieved via direct contact with a cryogenic fluid, forming a slurry with solid CO₂. The solid CO₂ is removed via filtration and warmed to produce liquid CO₂. This technology has been scaled up to 1 tCO₂/d treating flue-gas slipstreams from a variety of sources, achieving CO₂ capture between 95 and 99%.</p> <p>The CCC-ECL technology is being further progressed through a Department of Energy (DOE)-funded project.</p>	<p>Preliminary techno-economic assessment for CFG suggests a LCOE ~9 cents/kWh (c.f. ~11 cents/kWh for amine process)</p> <p>\$35/tCO₂ avoided estimated (c.f. \$69/tCO₂ avoided for amine process).</p> <p>Evaluation of ECL for a 550-MW coal-fired power station determined a parasitic power loss of 82.6 MW_e, or 0.74 MJ_e/kgCO₂.</p>	<p>Burt et al. 2009 Jensen et al. 2015 Sayre et al. 2017 Baxter et al. 2018</p>
CO ₂ freeze out in dynamically operated packed beds University of Twente University of Eindhoven Shell	<p>Flue gas supplied to previously refrigerated packed bed. Separation of CO₂ and H₂O from permanent gases achieved via differences in dew and sublimation points. Temperature and concentration fronts develop and move through the bed. This allows the removal of CO₂ and H₂O from the flue gas avoiding issues with plugging and pressure drop.</p> <p>Laboratory evaluation was able to achieve CO₂ separation from CO₂/N₂ mix.</p> <p>This process extended by Lively et al. (2012) who considered low-cost fibre beds as packing material.</p>	<p>Cooling duty required to capture 99% CO₂ from gas stream containing 10% CO₂ and 1% H₂O estimated at 1.8 MJ/kgCO₂. For a coefficient of performance of 50% (for refrigerator able to cool to –140 °C), this corresponds to electrical-energy requirement of 3.6 MJ_e/kgCO₂.</p> <p>Preliminary economic analysis completed for 600-MW coal-fired power plant (flue gas containing only CO₂ and N₂) showed similar cost of CO₂ avoided for MEA and cryogenic-based processes (~\$50/tCO₂ avoided).</p>	<p>Tuinier et al. 2010 Tuinier et al. 2011a Tuinier et al. 2011b</p>
Condensed rotational separation University of Eindhoven	<p>Rapid cooling of gas mixture to condensation temperature leads to a mist of fine droplets (1 to 10 micron). A rotational particle separator is then used to condense the droplets, allowing for separation of the condensed medium.</p> <p>To achieve 95% pure CO₂ with capture above 70–90% requires flue-gas CO₂ concentration in the range 40–70%. Hence technique should be used with upstream CO₂ concentrating step (e.g. membrane, oxyfuel).</p>		<p>van Benthum et al. 2010 Theunissen et al. 2011 van Benthum et al. 2012</p>
CO ₂ de-sublimation using Stirling coolers Tskuba University Tianjin University	<p>Water is removed from the flue gas in a first pre-cooling step. CO₂ is then removed in a freezing tower via de-sublimation. Frosted CO₂ is removed from the fins of the heat exchanger via a scraping rod.</p> <p>Experimental evaluation able to achieve 96% capture of CO₂ from simulated flue-gas stream with a cooling energy requirement of 1.6 MJ/kgCO₂.</p> <p>Heat integration anticipated to reduce power requirement by roughly 50%.</p>	<p>A preliminary economic analysis suggests total costs comparable to an MEA-based process.</p>	<p>Song et al. 2012 Song et al. 2012b Song et al. 2017</p>

TECHNOLOGY COMPANY/RESEARCH INSTITUTE	DESCRIPTION	COST AND ENERGY INFORMATION	REFERENCES
Centre for Energy and Processes ARMINES, France	<p>CO₂ captured by anti-sublimation on low-temperature surfaces at atmospheric pressure via an integrated cascade refrigeration cycle with a mixed refrigerant. Energy saving during defrosting and melting CO₂ (−130 to −100 °C).</p> <p>Due to low temperatures involved, power consumption sensitive to efficiency of cascade system. A laboratory-scale version has been successfully operated for about 7,000 h with a CO₂ capture rate ~10 kg/h.</p>	<p>Energy penalty for coal-fired power plant in the range 650–1250 kJ/kgCO₂ (4–9.9% penalty) for 90% capture of CO₂. Most of efficiency penalty due to power for compressors.</p> <p>Specific capture and compression work ~1.2 MJ/kgCO₂.</p> <p>Incremental COE 0.57–0.88 €cents/kWh_e, CO₂ mitigation cost 10–16 €/tCO₂ avoided.</p> <p>For gas-fired power plant, energy penalty in the range 820–1520 kJ/kgCO₂ (6–11.3% penalty) for 90% capture of CO₂.</p> <p>Incremental COE 0.7–1 €cent/kWh_e, CO₂ mitigation costs 17–24 €/tCO₂ avoided.</p>	Eide et al. 2005 Clodic and Younes 2003 Berstad et al. 2013
Inertial CO ₂ extraction system ACENT Laboratories Orbital ATK	<p>Uses cooling effect of supersonic expansion to cool flue gas, causing CO₂ in flue gas to form solid phase that can then be separated from gas stream.</p> <p>Remaining flue gas can be decelerated in diffuser to increase pressure allowing atmospheric pressure discharge. Solid CO₂ particles are pressurised via pumping, and melted to form liquid CO₂.</p> <p>Thermodynamic analysis suggests flue-gas preconditioning (increased pressure and/or lower temperature) required to achieve atmospheric pressure discharge.</p>		Berger et al. 2017

Development of cryogenic CO₂ removal processes is focusing on integration with liquefied natural-gas facilities. Expensive refrigeration can possibly be avoided when exploiting the cold duty available at gasification sites (Tuinier et al. 2010).

Discussion on commercialisation potential and development since previous review

In the previous review it was noted that the equipment required for this process consists largely of refrigeration systems and heat exchangers, which can be based on well-developed design and construction principles. Cyclic frosting and defrosting stages were expected to be a challenge that required demonstration at larger scale. At the time of the previous review, the principles had been evaluated in small-scale laboratory experiments, and the technology was determined to be at a TRL of 3, but with the potential for fast development and commercialisation.

The cryogenic CO₂ capture process being developed by Sustainable Energy Solutions has seen evaluation on flue-gas slipstreams, suggesting this technology has now progressed to a TRL of 5. The ongoing DOE/NETL-funded project is aiming at improving aspects of the process and progressing towards larger-scale demonstration. Alternate heat exchangers and solid–liquid separators are being assessed. Extended operation is still required to provide information on the potential corrosion from trace components in the flue gas.

2.5 Electrochemical separation

Electrochemical separation processes use differences in electrochemical potential to facilitate either the capture or release of CO₂. Concepts that have been explored include modified fuel cells, or application of electrochemistry to a standard liquid-based absorption plant. Electrochemical systems are often more efficient than thermochemical counterparts. Examples include aluminium production via the Hall–Heroult process, and water desalination via electrodialysis (Stern et al. 2013). Electrodialysis processes have also been considered for the reclamation of degraded amines (Garg et al. 2018) and for regeneration of CO₂-loaded sorbents (Taniguchi and Yamada 2017). Electrochemical cycles are also being explored for the capture of CO₂. These systems exploit the responsiveness of the thermodynamic equilibrium of CO₂ hydration to small pH changes (Rheinhardt et al. 2017). Combining CO₂ capture with batteries as a means of storing CO₂ is also being explored (Chandler 2018). A summary of research in this area is provided in Table 21.

Table 21 Electrochemical separation technologies

TECHNOLOGY COMPANY/RESEARCH INSTITUTE	DESCRIPTION	COST AND ENERGY INFORMATION	REFERENCES
Gas-fuelled molten carbonate fuel cell Combined electric power and carbon dioxide separation system FuelCell Energy	<p>Uses electrochemical membrane technology where the driving force for separation is the electrochemical potential and results in simultaneous power production and CO₂ separation. The membrane consists of ceramic-based layers filled with carbonate salts, and separates CO₂ from flue gas with 100% selectivity and fast kinetics.</p> <p>In-situ steam reforming at anode to produce H₂. CO₂ reacts with O₂ to form carbonate ions at cathode. Carbonate ions travel to anode where they are reduced to CO₂ and H₂O. If cathode is supplied with CO₂ source (e.g. flue gas), CO₂ can be separated at anode.</p> <p>Cell durability has been assessed at the bench scale for potential contaminants S, Cl, Hg and Se. While voltage was noted to drop with an increase in SO₂ concentration, this was recovered once SO₂ levels were reduced back to design levels. 250-cm² cell evaluated at bench scale with synthetic flue gases. 92% CO₂ separation achieved with a CO₂ flux rate of 128 scc/s/m² and complete selectivity of CO₂ transfer from the cathode to the anode. ECM stack, with total area of 11.7 m², evaluated at bench scale. CO₂ flux of 116 cc/s/m² was maintained over 6,500 h, transferring >90% of the CO₂ from the cathode to the anode. DC power output nearly constant at 8 kW, and experienced power degradation rate of 0.05%/1000 h.</p> <p>In current DOE-funded project, a 3-MWe pilot (60 t/d) will be designed and constructed, and operated for at least 2 months on a flue-gas slipstream from the Barry Generating station.</p>	<p>Economic analysis based on DOE case 9 (90% capture from 550-MW sub-critical coal-fired power station). Required 1792 ECM stacks separated into eight sections. ECM stacks generated an additional 351 MW power. Efficiency 38.8% (higher heating value) (c.f. 36.8% for base plant).</p> <p>Capture cost \$33.6 USD/t, 35% increase in cost of electricity (COE). Cost of CO₂ avoided 26.7 \$2007/tonne.</p> <p>LCOE 102.6 mills/kWh (\$2007) (c.f. 75.3 for base plant).</p> <p>Can be integrated into NGCC power plant between gas turbine exhaust and heat recovery steam generator. Specific primary energy consumption for CO₂ avoided of 1.3 MJ/kgCO₂ (c.f. 3-3.5 MJ/kgCO₂ for liquid absorption based capture). Cost of CO₂ avoided €33-44/tCO₂ (cost range dependent on whether projected or current fuel cell costs used)</p> <p>Analysis by Wood (2018) suggests LCOE £68/MWh and cost of CO₂ avoided £76/tCO₂ (c.f. LCOE £67/MWh and £73/tCO₂ avoided for NGCC with PCC)</p>	<p>Lockwood 2016 Ghezel-Ayagh et al. 2017 Eisler 2018 NETL 2018i Spinelli et al. 2015 Wood 2018</p>

TECHNOLOGY COMPANY/RESEARCH INSTITUTE	DESCRIPTION	COST AND ENERGY INFORMATION	REFERENCES
PureStream CWx Future Environmental Technologies	Flue gas blended with sea water or power plant waste water. CO ₂ converted to soluble carbonates and bicarbonate under applied voltage in electrochemical cell.	Claims 40% less capital expenditure than state-of-the-art CCS, 6% reduction in operating costs.	Lockwood 2016
Absorption Enthalpy Converter CSIRO	Uses the ligand capability of many amines. Amines (including NH ₃) are able to form complexes with many metals, dissolving them into solution. These complexes can then be reversed by the introduction of CO ₂ into the solution, resulting in the deposition of the metal. This forms the basis of an electrochemical cell, converting the absorption enthalpy into power. Laboratory-scale evaluation identified Cu as a preferred starting material for the enthalpy conversion process using NH ₃ . Battery discharge experiments showed an energy output of 4.1 kJ/molCO ₂ , resulting in an enthalpy-to-electricity conversion of 6.4%.		Li et al. 2018
Electrochemically mediated amine regeneration MIT	Modulates amine affinity for CO ₂ via redox responsive molecules. Lean/rich cross heat exchanger and stripping column replaced by electrochemical cell. Potential for higher CO ₂ desorption pressures, smaller absorbers, lower energy demand. Regeneration can achieve lower lean loadings in amine, leading to lower circulating absorbent flow rates compared with thermal regeneration. Metal ion added to amine solution, forming complex with amine. Care needed to select amines whose metal complex does not precipitate.	Experimental results indicate open-circuit efficiency of 54% (15 kJ/mol CO ₂) achievable. Bench-scale unit regenerated CO ₂ requiring <100 kJ/molCO ₂ at ambient conditions. Improved performance expected with operation at higher temperatures and pressures. Further analysis suggests can generate CO ₂ for transportation at <50 kJ/mol CO ₂ .	Stern et al. 2013 Eltayeb et al. 2014

Discussion on commercialisation potential and development since previous review

The previous review considered the case for electrochemically mediated amine regeneration. They noted that an electrical-energy consumption of 100 kJ/mol for regeneration would equate to nearly 6 GJ/tCO₂ in thermal energy, which compares unfavourably with the energy requirement of the standard CO₂ capture process. At the time of the previous review, bench-scale proof of concept had been achieved, and the technology was determined to have a TRL of 1. It appears that some additional laboratory evaluation has continued since the previous review; however, the TRL is comparable that determined previously.

Perhaps of more interest is the recent work applying fuel-cell processes. As with most fuel-cell applications, the processes will require very clean flue gases, necessitating an upstream caustic scrubber, particulate removal and mist eliminators. In their review, Lockwood (2016) noted that standard fuel cells (without the ability to capture CO₂) have already been scaled up in modular units for power-generating plant of up to 60 MW. A more detailed analysis of fuel cell integrated with CCS

is pending with the IEAGHG (Chronopoulos et al. 2018). The planned demonstration of FuelCell's technology at Plant Barry will progress this technology to a TRL of 6.

2.6 Microbial, microalgae

Biological CO₂ capture processes use CO₂ to promote plant or algae growth. For algae-based CO₂ capture, the processes that show the most promise are open-raceway algal ponds (Cowan et al. 2011) due to the current high cost of photobioreactors (Zhang 2015). Typically the algae harvested are intended for subsequent use as stock feed, biofuels production, food dyes or nutraceuticals, or simply to be co-combusted in the power plant. Capture of CO₂ from combustion flue gas for direct use in algae production has been widely investigated and has been applied commercially (Cowan et al. 2011). However, as highlighted in the previous review, using algae-based systems to capture CO₂ from a power-station flue-gas requires significant area, and thus far process economics have not proved favourable for this technology as a CO₂ mitigation method.

The University of Kentucky have photobioreactors installed at the East Bend power station. They were able to achieve an algal production rate of 35 g/(m².day). A lifecycle analysis confirmed the technology could be considered a CO₂-capture technology. A techno-economic assessment showed the cost of producing algae to be \$875/t. Ongoing work is evaluating the potential to generate bioplastics as a high-value product (Crocker 2017).

MicroBio Engineering has evaluated algae production using their algae raceway ponds installed at Stanton Energy Centre power station (Benemann et al. 2018). They completed a site-specific techno-economic assessment using the algae as feed to the power plant, for renewable natural gas and as animal feed. Animal feed was the most economic case, provided the feed could be sold for \$890/Mg (c.f. \$393/Mg for soybeans).

Michigan State University, in partnership with PHYCO₂, are evaluating a process that combines biological and chemical processes to capture CO₂ from flue gas. The process produces amino-acid absorbents, polyurethanes, biodiesel and methanol. Photobioreactors have been installed at the TB Simon power plant, and a techno-economic assessment is currently under way (Liao, 2018).

Helios-NRG and The State University of New York at Buffalo are undertaking a project to develop a multi-stage continuous-flow photo-bioreactor for high growth rate microalgae. The algae is used to capture CO₂ from flue gas before being concentrated and used for the production of high-value chemicals and nutraceuticals, with the remaining algae converted to biofuel (NETL 2018c).

Demonstration of algae-based CO₂ capture has also been achieved at Bayswater Power Station (Algae Tec, Australia), Tarong Power Station (MBD Energy, Australia), Duernrohr Power Station (EVN, Austria), Penglai Power Station (Yantai Hairong Biology Technology, China), Da-Lin Power plant (Taiwan Power Research Institute, Taiwan), Hamburg-Reitbrook Power Station (EON, Germany), Niederaussem Power Station (RWE, Germany), Senftenberg Power Station (Vattenfall, Germany), Angul Captive Power Plant (NALCO, India) and Rutenberg Power Station (Seambiotic, Israel) (Zhang 2015).

Discussion on commercialisation potential and development since previous review

As highlighted in the previous report, due to the scale required, the economics of biological processes to capture the significant volumes of CO₂ produced from power stations are currently

unfavourable. As a result, this technology was assessed as being at a TRL of 1 in the previous review. CO₂ capture using algae from combustion flue gases has now been evaluated treating slipstreams of coal flue gases at several power plants worldwide. However, these projects have still not overcome the issue of the low capture rates, and unfavourable economics despite the current focus on high-value products. Most of the existing processing technologies are adapted from processes used in the food, biopharmaceutical and waste water industries, and as such are not necessarily adapted for algae production using flue gases. Even though pilot-scale evaluation treating flue-gas slipstreams has been achieved, a viable method for reducing CO₂ emissions from power stations has not been demonstrated. As such, this technology is assessed as being at a TRL of 4.

2.7 Direct air capture

Direct air capture (DAC) was not considered in the previous review. It is gaining significantly more attraction today, however, particularly as the need for negative emissions technologies becomes more pressing. It has high flexibility in choice of location, which lends itself to opportunities such as integration with renewable and solar energy sources. Based on the low CO₂ partial pressure in the atmosphere, DAC of CO₂ is thermodynamically unfavourable. In addition, the large volumes of air that require processing suggests processes with low pressure drop are essential. Due to the dilute nature of CO₂ in the atmosphere, chemical sorbents with strong CO₂-binding affinities are typically employed. Processes considered for DAC include absorption into aqueous alkaline absorbents (particularly NaOH, KOH and Ca(OH)₂), and porous, solid-supported amines (Brethome et al. 2018, Stolaroff et al. 2008). The capture of CO₂ from ambient air was commercialised in the 1950s as a pre-treatment for cryogenic air separation (Keith et al. 2018), and is also used for treating air in submarines and spacecraft (Goeppert et al. 2011). However, the flow rates treated by these commercial systems is significantly lower than the volumes that would require treatment for climate change mitigation purposes.

While aqueous-amine processes are the leading technology for CO₂ capture from industrial sources, they are less favourable for DAC applications, due to the large energy requirement and high absorbent losses as a result of the large volume of air that requires processing. Minimising sorbent loss while maintaining the capture efficiency of amines can be achieved using amine-impregnated solid sorbents. The type of amine contributes significantly to the adsorption capacity of the material, and primary amines have been found to perform most effectively under DAC conditions. The Technical Research Centre, Finland, have evaluated a polystyrene functionalised with a primary amine in the laboratory under DAC conditions (Elfving et al. 2017). Amine-impregnated solid sorbents have also been evaluated by the University of Southern California (Goeppert et al. 2011), and amine-based nanofibrillated cellulose has been evaluated by ETH and Climeworks (Gebald et al. 2011, Sehaqui et al. 2015). Amine-impregnated MOFs have been evaluated by the Georgia Institute of Technology (Darunte et al. 2016). To maintain low pressure drop for solid sorbents, monolithic structures have been proposed. The University of Twente have evaluated hydrated K₂CO₃ supported on an activated-carbon monolith as a low-pressure drop solid sorbent for the capture of CO₂ from air (Rodriguez-Mosqueda et al. 2018). Regeneration used an air flush, generating CO₂-enriched air for use in e.g. greenhouses. Salt content was only 0.0558 g_{K₂CO₃}/g_{adsorbent} due to the deterioration of the carrier at higher loadings.

One of the earlier methods for capturing CO₂ from air used hydroxide solutions. The CO₂ reacts with the hydroxide, forming carbonates that are subsequently precipitated out of solution as calcium carbonate through the addition of calcium oxide. The carbonate then needs to be regenerated via calcination at temperatures around 900 °C at atmospheric pressure. Oxyfuel combustion is typically used for this step to avoid an additional separation step (Shimizu et al. 1999). A similar process is required for processes involving other alkali hydroxides. Zeman (2007) calculated the energy consumption of a capture process using sodium hydroxide to be 350 kJ/molCO₂, with the thermal energy of the calciner and mechanical power for air movement dominating. Stolaroff et al. (2008) evaluated a process using a sodium hydroxide spray to capture CO₂. Water loss from the system could be significant, and thus careful design was required. CO₂ capture costs of \$96/tCO₂ (range \$53–127/tCO₂) were estimated for this system. Ohio State University are developing a membrane process to capture CO₂ from sources containing <1% CO₂. This is currently being developed as an add-on to a standard CO₂-capture technology for additional CO₂ removal, increasing capture rates. This technology has been covered in more detail in the membrane section of this report (Ho et al. 2017). Oak Ridge National Laboratory (Brethome et al. 2018) has developed a process for air capture where CO₂ is absorbed into aqueous amino-acid solutions (glycine and sarcosine) using a household humidifier. The CO₂-loaded solutions are then reacted with a guanidine compound, which crystallises an insoluble carbonate salt, regenerating the amino acid. CO₂ is recovered from the guanidine compound using concentrated solar thermal power (80–120 °C). This has been demonstrated at proof-of-concept stage in the laboratory.

One of the more advanced air-capture technologies is that developed by Carbon Engineering. Carbon Engineering's technology uses potassium hydroxide solution coupled with a calcium caustic recovery loop to capture CO₂ from air or other dilute sources. The potassium carbonate solution produced is regenerated using calcium hydroxide, producing calcium carbonate pellets. The pellets are then calcined (in an oxy-fired calciner), producing a pure CO₂ stream and CaO, which is hydrated to regenerate the calcium hydroxide. When CO₂ is delivered at 15 MPa, 8.81 GJ of natural gas (or 5.25 GJ gas and 366 kWh electricity) are required per ton CO₂ captured (Keith et al. 2018). A study completed with the Harvard Business School suggests CO₂-capture costs from air of \$100/tCO₂. Levelised cost per ton CO₂ captured is in the range \$94–232/tCO₂ (Keith et al. 2018). Carbon Engineering have developed a 1 tCO₂/d pilot facility (operating since 2015), and are currently further advancing the technology readiness through a DOE-funded project (NETL 2018d). They are also coupling their technology with electrolysis to use the CO₂ to generate liquid fuels. Carbon Engineering have increased the commercialisation potential by either identifying commercial hardware that meets the process specification, or identifying commercial hardware that can be adapted, for each unit operation in the process. As an example, the contactor is based on commercial cooling-tower technology, while the pellet reactor is adapted from commercial water-treating technology.

Another air-capture technology that has seen significant development is that being developed by Climeworks. Their technology draws air through a solid-sorbent filter that captures the CO₂. Once saturated, low-grade heat (100 °C) is then used to release the CO₂ and regenerate the filter (Climeworks 2018). Climeworks currently operate 3 DAC plants. The first began operation in Zurich in 2017, capturing 900 tCO₂/annum. The regeneration step of this facility, however, uses an air stream, with the CO₂-enriched air used in greenhouses. A 50 tCO₂/annum plant is operating near a geothermal plant in Iceland, with the captured CO₂ reinjected underground with water, where it

reacts with the basalt rock. A 150 tCO₂/annum plant recently began operations in Troia, Italy. The CO₂ from this facility is combined with H₂ generated via electrolysis for the production of methane. Initial economic estimates by Climeworks suggested CO₂-capture costs in the range \$600–800/tCO₂ (Rathi, 2018).

Global Thermostat's first direct air capture pilot plant was built at SRI International's Menlo Park facility in 2010 (1,000 tons/annum). More recently a commercial scale (4000 tons/annum) facility has been constructed in Huntsville, Alabama. Global Thermostat's technology uses a honeycomb monolith coated with an aminopolymer sorbent. Sorbent regeneration is achieved using low cost process heat (e.g. steam at 95 °C), with CO₂ capture costs as low as \$50/tCO₂ suggested (Chichilnisky and Eisenberger 2011, Chichilnisky 2018).

Discussion on commercialisation potential and development since previous review

Small-scale DAC installations are already operational, as evidenced by Climeworks and Carbon Energy's facilities in particular, suggesting that the technology is at a TRL of 5. Commercial applications, however, seem some way off, and likely will not become a reality until some form of carbon price becomes available. The current plants have focused on using standard technologies where possible, making future scale-up of these processes more straightforward.

There is still significant uncertainty in estimating the costs of DAC processes, with costs in the range \$30–1000/tCO₂ reported (Sanz-Perez et al. 2016). One of the more rigorous cost studies completed was that by the American Physical Society, which suggested \$600/tCO₂ for a system using aqueous NaOH as the capture agent (APS 2011). More recent studies completed by Harvard Business School for the Carbon Engineering system are suggesting costs closer to \$100/tCO₂ (Keith et al. 2018).

It is unlikely that DAC will be a replacement for CO₂-capture technologies employed directly at CO₂ emitters. As highlighted in APS (2011), to capture the CO₂ emitted from a 1000-MW power station would require a DAC system in the order of 10 m high and 30 km long. Thus, deployment of DAC systems is only likely after nearly all significant point sources of fossil CO₂ emissions are eliminated, either by substitution of non-fossil alternatives or by capture of nearly all of their CO₂ emissions. Nonetheless, DAC is one of a small number of strategies that might enable the world to reduce the atmospheric concentration of CO₂ (APS 2011) resulting from legacy emissions, and diffuse CO₂ emission sources not amenable to other CO₂-capture technologies.

3 High-temperature solids-looping processes

This section covers two types of high-temperature solids-looping processes: calcium-looping processes and chemical-looping combustion.

3.1 Calcium-looping processes

PCC via calcium (Ca) looping uses calcium oxide (CaO) as a regenerable CO₂-capture sorbent. Flue gas from the power plant is brought into contact with a fluidised bed of CaO, which reacts with CO₂ to produce calcium carbonate (CaCO₃) at temperatures around 650 °C. The CaCO₃ is conveyed to a separate, fluidised-bed reactor where it is regenerated. A flow diagram of a typical Ca-looping process is provided in Figure 10. Due to the formation of calcium carbonate, the process is also known as the carbonate-looping process (Lasheras et al. 2011). One of the main challenges of Ca-looping processes is the high calcination enthalpy of CaCO₃ (168 kJ/mol at 900 °C). This requires a large heat input to regenerate the CaO sorbent, and it is intrinsically difficult to supply a large heat flow to a high-temperature reactor (Abanades et al. 2015). To achieve this, oxyfuel combustion is typically used.

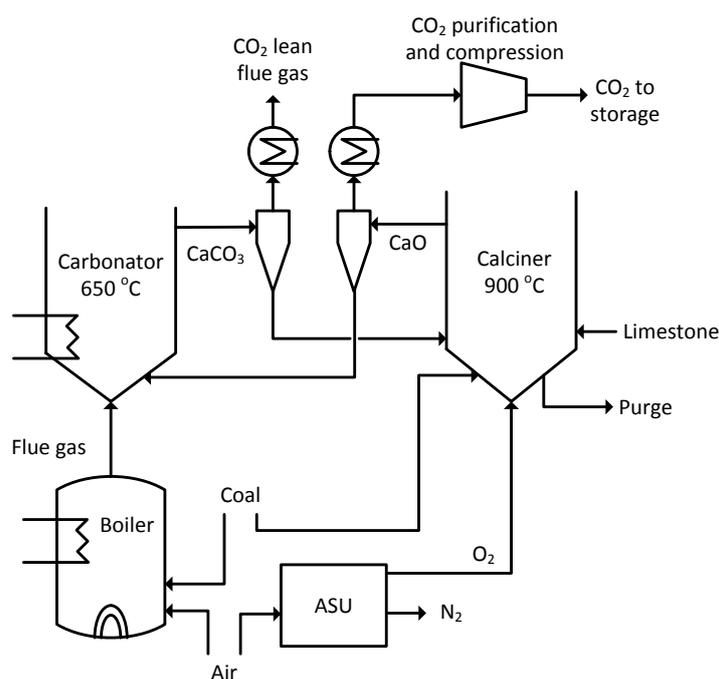


Figure 10 Flow diagram of calcium looping process for CO₂ capture from power plant flue gas (Abanades et al. 2015)

Degradation of the CaO sorbent is another challenge for the process. CaO particles are prone to sintering at the high temperatures typically required for calcination. The percentage of active CaO has been shown to drop rapidly over tens of process cycles, reducing its effectiveness for CO₂ capture. However residual calcium conversions of 0.06-0.1 have been achieved after many hundreds of cycles, which allows effective capture with sufficient solid circulation rates (i.e. with Ca/C ratios of 10-20). In addition, attrition losses of active CaO, sulfation of CaO and ash build up (from the fuel used in the calciner) require a continuous flow of crushed limestone to maintain capture efficiency.

Pre-treatment and activation steps have also been developed in an attempt to reduce the decay in sorbent reactivity. If SO_2 is present in the flue-gas stream, it will also be captured by the process, forming CaSO_4 . As CaSO_4 requires temperatures in excess of $1450\text{ }^\circ\text{C}$ to decompose, it will build up in the process. As a result, a purge stream of solids is continuously removed from the system.

A benefit of the process is the high operating temperature of the reactors, which allows for additional steam generation by recovering part of the energy introduced with the fuel fed to the calciner. This then allows a large fraction of the heat input to the calciner to be transferred to additional power generation, reducing the overall energy penalty of the process (Arias et al. 2017). Overall efficiency penalties as low as 5% are theoretically attainable (Lockwood 2016). Additional advantages of the Ca-looping concept include: use of low-cost, widely available absorbent (limestone); flue gas does not require pre-treatment (SO_2 removal); environmentally benign nature of CaCO_3 ; opportunities for operation flexibility and load following through stockpiling CaO and CaCO_3 ; and the possibility of using waste sorbent in the cement industry (Lockwood 2016, Criado et al. 2017).

Several reactor types have been considered for the carbonator and calciner. Due to development of circulating, fluidised-bed combustors, circulating fluidised beds are commonly used. These reactors also allow higher heat and mass-transfer rates, and good gas–solid interactions. Other advantages include capability for continuous operations, applicability over a wide range of particle properties, geometric simplicity, and suitability for large-scale operation. Bubbling fluidised beds and rotary kilns have also been proposed. These reactor types however have limitations regarding gas flows to prevent solids entrainment and temperature profiles (in the case of rotary kilns). Rotary kilns have already found widespread application as calciners in the cement industry (Change et al. 2013). However, it is expected that carbonation reactors will need to accommodate large superficial gas velocities ($>3\text{ m/s}$) to have reasonable cross-sections. As such, circulating fluidised beds and entrained flow reactors are considered most suitable for the carbonator (Romano et al. 2014, Abanades et al. 2015, Spinelli et al. 2017).

Spent material (mostly CaO) can be used in cement manufacture (Dieter et al. 2013). Measured attrition rates (Dieter et al. 2013) were lower than the limestone make-up rates required to maintain adequate bed material for high CO_2 -capture rates. Chang et al. (2013) similarly measured solids carried over with vent gas as a measure of attrition and bed loss. This was found to be approximately 20% of the bed material after a 100-h test. This attrition rate was found to be similar to the CaO make-up rate required to replace bed inventory as a result of sintering and deactivation.

Ca-looping technologies are being progressed by several researchers, power and cement companies worldwide. This has led to the development and operation of several pilot-scale facilities, a summary of which is provided in Table 22.

Table 22 Summary of calcium-looping technologies for post-combustion capture of CO₂ evaluated at pilot scale

TECHNOLOGY COMPANY/RESEARCH INSTITUTE	DESCRIPTION	COST AND ENERGY INFORMATION	REFERENCES
La Pereda 1.7-MW _{th} plant located at Hunosa circulating fluidised-bed combustion (CFBC) coal plant, Spain CaOling (2009–2013) ReCaL (2012–2015) CaO ₂ (2014–2017) Spanish research council Hunosa Endesa regeneration	Comprises two circulating fluidised beds (CFBs): oxyfuel-fired calciner (0.75 x 15 m) and carbonator (0.65 x 15 m). Double-loop seals operating in bubbling fluidised bed mode to control solids movement. Achieved 90% CO ₂ capture and 95% SO ₂ capture (if lime added). Evaluated two process improvements. Reactivating partially carbonated sorbent in concentrated CO ₂ (>60%) to minimise deactivation (recarbonator, T >750°C). Performing oxyfuel in higher concentration O ₂ (up to 75% O ₂) reducing heat requirement and size of calciner and air-separation unit (ASU).	Economic analysis as part of Caoling project identified 20–25 €/tCO ₂ captured. Increasing O ₂ content in calciner (minimising CO ₂ recycle) thought to reduce calciner/ASU costs by around 25%.	Lockwood 2016 Arias et al. 2017 Arias et al. 2018 Diego et al. 2016 Endesa 2014 Abanades et al. 2015
300-kW _{th} test facility 1-MW _{th} pilot Technical University of Darmstadt	Pilot facility contains 0.6 x 8.6 m carbonator, 0.4 x 11 m calciner. Recently upgraded to operate with coal combustion flue gas and calciner in oxyfiring mode. A screw conveyor is used to carry material from the carbonator to the calciner, and a loop seal for the return route. Duration operation achieved 1200 h operation with steady-state periods of up to 60 h. CO ₂ -capture efficiencies of over 95% achieved. The effect of fuel type to the calciner and sorbent particle size also evaluated. Recent EU Scarlet project acquired information needed to design 20-MW _{th} facility. 300-kW _{th} test facility used to evaluate indirectly heated calciner, where heat pipes are used to transfer heat between combustor and calciner. 90% CO ₂ capture achieved, but heat transfer lower than anticipated.	Results of Scarlet project suggest net efficiency loss for CO ₂ -capture (including compression) of 6–7% points for hard coal and lignite plants. Cost of CO ₂ avoided 20–27 €/tCO ₂ . Economic evaluation of indirectly heated calciner suggests CO ₂ -avoidance cost of 22.6 €/tCO ₂ (c.f. 27 €/tCO ₂ for standard Ca-looping plant).	Hilz et al. 2017 Hilz et al. 2018 Scarlet 2017 Reitz et al. 2016 Junk et al. 2016 Scarlet 2018
3-kW _{th} test facility 1.9-MW _{th} pilot Industrial Technology Research Institute, Taiwan	3-kW _{th} test facility with bubbling fluidised bed carbonator and rotary kiln calciner. Moving bed used initially for calciner. Found to be difficult to operate, and changed to kiln calciner. Liquefied petroleum gas fuel used for calciner. 1.9-MW _{th} calcium-looping pilot in which the calciner takes the form of a rotary kiln, aiming to further demonstrate the compatibility of the process with cement production. Calciner is oxy-fired diesel. Treats flue gas (CO ₂ >15%) from cement plant. Achieved 300 h fully looping continuous process. Despite oxyfiring, CO ₂ concentration at outlet of kiln only 13.7% due to air leakage.		Chang et al. 2013 Chang et al. 2014 Lockwood 2016
200-kW _{th} duel fluidised-bed pilot plant University of Stuttgart	Two 0.2 x 10 m refractory-lined CFB reactors. Calciner oxy-fired with wood pellets (50% O ₂) or hard coal. Sorbent loss (measured by dust carryover) <5wt% of inventory per hour over 1 week of operation. Operated with synthetic flue gas. CO ₂ -capture efficiencies >90% achieved for several operating conditions. Recent experimental work evaluating Ca-looping conditions relevant to integration with cement plant.		Dieter et al. 2013 Hornberger et al. 2017

TECHNOLOGY COMPANY/RESEARCH INSTITUTE	DESCRIPTION	COST AND ENERGY INFORMATION	REFERENCES
75-kW _{th} pilot plant CanmetENERGY, Natural Resources Canada	CFB calciner at 900 °C and bubbling bed carbonator at 650 °C Flue gas supplied from natural-gas combustor. Oxyfuel combustion in calciner using wood pellets. Calciner 0.1 x 5.1 m, carbonator 0.1 x 3 m. Sorbent characteristics evaluated. Capture efficiency noted to decrease from 95–70% after 25 cycles. Significant loss of bed material noted due to attrition (no sorbent make-up used). More recently evaluated CaO-based pellets. Under conditions evaluated, pellets noted to sinter and performance comparable to cheaper limestone.		Lu et al. 2008 Symonds et al. 2016
30-kW _{th} test facility 300-kW _{th} pilot located at coal power station Spanish Research Council INCAR-CSIC	Pilot developed to capture CO ₂ in-situ. Two 0.4 x 12 m CFB. Biomass combustion in fluidised-bed combustor/carbonator at 700 °C. Biomass also used as fuel for calciner. CO ₂ -capture efficiencies 70–95% achieved. Both carbonator and calciner operated with air. 100 h steady-state operation achieved. Narrow operating temperature window required in combustor/carbonator 30-kW _{th} test facility contains 0.1 x 6.3 m carbonator, 0.1 x 6.1 m calciner. Recently used to evaluate attrition rates of commercial limestone.	43 €/tonne (2009) CO ₂ avoided (84% overall capture, includes a compression and purification unit producing 95% pure CO ₂). Cost of CO ₂ avoided slightly lower than the cost of stand-alone oxy-fired system burning biomass. Cost of electricity (COE) 132 €/MWh. O ₂ consumption about 1/3 of the equivalent oxy-fired system burning the same total flow of biomass and fuel.	Alonso et al. 2014 Ozcan et al. 2014 Alonso et al. 2018
120-kW _{th} sub-pilot system Ohio State University	Electrically heated rotary kiln calciner. 90% CO ₂ and 100% SO ₂ removal from the flue gas achieved. Addition of hydrator to improve CO ₂ adsorption capacity and maintain reactivity.		Wang et al. 2010
Calix Calix Limited Australian National University	Endex process couples heat transfer between the exothermic carbonation and endothermic calcination steps, with carbonation occurring at higher temperature than calcining process. Minimises sintering and deactivation of CaO sorbent. In theory, CO ₂ removal can be achieved without additional heat input. Vacuum used to maintain low CO ₂ partial pressure in calciner. Challenging heat transfer to calciner, and circulation of solids to reactors at different pressures. Being progressed for application to cement manufacture through the LEILAC project with demonstration plant to be constructed at the Heidelberg cement plant in Lixhe, Belgium. Standard cement plant calciner to be replaced by Calix indirectly heated calciner. Technology similar to MgCO ₃ process already operating using 45-m reactor (Ballarat, Australia).	Removal of requirement for external heating believed to significantly reduce cost of CO ₂ capture. CO ₂ capture <15 €/tCO ₂ estimated.	Ball and Sceats 2010 Carbon Capture Journal 2009 LEILAC, 2017

Mantripragada and Rubin (2014) completed a techno-economic assessment of a conventional Ca-looping process applied to a 650-MW supercritical coal-fired power station. They considered the Ca-looping plant to be first of a kind and compared its economic performance to a standard CO₂ absorption plant using MEA. Capital costs of the reactors were based on the costs of circulating fluidised bed (CFB) boilers/gasifiers. To supply the heat required for the calcination reactor, 170 t/h coal was needed for the oxycombustion (c.f. 182 t/h coal used in the base plant). This required a boiler of similar scale to the base plant, and roughly doubled the amount of CO₂ to be captured. The

CO₂ product was predicted to be ~93% pure, and thus required an additional CPU to reach pipeline specifications (~99% purity). The solid waste stream from the process was estimated to be more than 200 t/h. It was found that the Ca-looping process achieved a lower efficiency penalty than the MEA-based capture unit (base plant without PCC 39 % (HHV), with Ca looping 36%, with MEA 28%); however, the capital costs and cost of electricity were higher (LCOE base plant \$59/MWh (USD 2012), with Ca looping \$140/MWh, with MEA \$95/MWh) as the capital cost of the calcium looping sub-system necessarily includes the power generation equipment to generate additional power from the high temperature heat sources (calciner gas and solid outputs at T >900°C and carbonator at 650°C). The cost of CO₂ avoided was calculated at \$105/tCO₂ for the Ca-looping process. The authors note that one of the reasons for the high capital cost for the Ca-looping process was due to the application of a high process-contingency cost factor, resulting from the assumption of the plant being first of a kind. If they applied a smaller contingency (around 5%), this would bring the capital cost and LCOE close to the MEA-based process. They suggest small benefit would be received from selling the waste sorbent (as the process is capital intensive), with larger cost reductions expected through process improvements, such as heat integration, indirect heating, or using natural gas instead of coal in the calciner. Lockwood (2016) also highlighted indirect heating as a method to be investigated for improving the efficiency of the process through eliminating the need for the air-separation unit (ASU).

As many parts of the Ca-looping process are already well established (circulating fluidised-bed combustion [CFBC], steam cycle to recover thermal outputs from the system, ASU, CPU), Abanades et al. (2015) estimated the cost of a Ca-looping system based on it being an nth of a kind plant. Cost information was sourced by adapting the cost of these components from a DOE cost analysis completed for an oxyfuel combustion plant. A separate cost estimate was used for the refractory-lined calciner, as it is a newer technology. The calciner was assumed to be similar to a CFBC mineral roaster, and of similar scale to refractory CaCO₃ pre-calciners used in cement plants, for which cost information exists. The analysis by Abanades et al. (2015) resulted in an overall efficiency penalty of 6.2%, a cost of \$40/tCO₂ avoided, and a cost of electricity increase of 43% over the reference plant.

More recent focus has been on the application of Ca-looping technologies to the cement industry. This is being progressed in Europe through the CEMCAP and CLEANKER projects. In CEMCAP the overall aim of one part of the project is the demonstration of Ca-looping under conditions relevant to cement plants. This will be achieved via long-term experimental campaigns to be completed at the 200-kW_{th} pilot plant at the University of Stuttgart. Screening of suitable sorbents is being provided by the Spanish National Research Council (CSIC) using their 30-kW_{th} test facility. Politecnico di Milano will be providing simulation of the full-scale process (CEMCAP 2018, Spinelli et al. 2017). The CLEANKER project aims to demonstrate the technology for application to cement plants, and to progress the technology to a TRL of 7. The main objective of the project is the demonstration of the technology at a cement plant in Italy (CLEANKER 2018).

Discussion on commercialisation potential and development since previous review

Ca-looping technologies are more likely to be applied as a retrofit technology to a pre-existing coal-fired power plant. They would be particularly applicable to areas where an increase in generating capacity is also required. They are, however, less applicable to NGCC, and other gases with low CO₂ concentrations (Berstadt et al. 2013). The production of CaO as a purge suggests the technology will have good application in the cement industry. The main differences between Ca looping applied

to the cement industry to that developed to date under PCC conditions are the high CO₂ load sent to the carbonator (higher CO₂ concentration in the flue gas) when the Ca-looping plant is retrofitted to an existing cement plant. This is however not favourable, because it translates into a double calcination (CO₂ evolves first from the calcination of CaCO₃ in the cement plant and then is captured again as CaCO₃ to be again calcined in the Ca-looping calciner). Integrated solutions with a single calciner are inherently more efficient (Romano et al. 2014, Spinelli et al. 2017). The use of sorbents with a higher activity as a consequence of the larger limestone make-up flows being used in the calciner (Arias et al. 2017) has been recently evaluated within the CEMCAP project on a 30-kW_{th} pilot plant. They concluded that the technology can be retrofitted by integrating the Ca-looping system to cement facilities on the basis of knowledge acquired through evaluation for PCC.

The scale-up prospects of Ca-looping systems for PCC of CO₂ are generally considered to be good. Significant large-scale pilot demonstration has already been achieved. In addition, several of the process stages required, such as air separation, CO₂ purification, circulating fluidised beds combustors and calciner, additional boiler equipment to recover thermal energy from high temperature sources etc, have already been commercialised at similar scales in other industries. Where the carbonator and calciner are CFB reactors, many of the key elements (risers, cyclones, return legs and loop seals, heat-transfer equipment, structural components and materials) can use learning achieved in commercial CFBC power technology (Abanades et al. 2015). A 30-MW_{th} oxyfuel pilot has been operated since 2011, and a FEED study has been completed by Foster Wheeler and Endesa for the 300-MW Compostilla plant. Conventional air-fired CFBC has been widely demonstrated for plants up to 600 MW (Lockwood 2016). While CO₂ product clean-up may be required, it will be comparable to that already used in other oxyfuel processes.

Based on the operation of the 1.7-MW_{th} La Pereda pilot plant, Ca-looping technologies were assessed as being at a TRL of 6 in the previous review (IEAGHG 2014). Since then, some of the efficiency improvement concepts suggested (e.g. high O₂ firing, external heating, CaO reactivation by recarbonation) have now been evaluated at pilot scale, suggesting these too are now at a TRL of 6. In their review, Abanades et al. (2015) noted that oxy-fired fluidised-bed combustor used under calcination conditions as being highly developed (TRL 7-8), while the core of the system, an interconnected carbonator–calciner reactor system with continuous solids circulation, had been evaluated at TRL 5–6 level. Where biomass co-firing is applied, Foster Wheeler’s 300-MW bio CFB boiler concept generates steam at 568/566 °C and 179/43.6 bar, and is considered market ready (Ozcan et al. 2014).

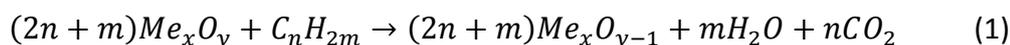
Ongoing research is expected to focus on improving the stability of the circulating sorbent material, investigating integration methods, and removing the requirement for oxy-fired regeneration through using indirect heating. Improving sorbent stability will lower make-up requirements and the amount of circulating sorbent material. As the air separation required for oxyfuel and compression of CO₂ are the two largest contributors to the energy requirement, reducing these stages through enhanced efficiency concepts is anticipated to have significant savings potential.

3.2 Chemical-looping combustion

Chemical-looping combustion (CLC) is a two-step energy conversion process where the fuel and air reactors are separated. An oxygen carrier (OC) is used to transfer O₂ from the air reactor to the fuel reactor. This allows the fuel to react with the oxygen, producing a highly concentrated CO₂ stream.

Metal oxides (and some sulphides like CaS) are typically used as the OC. During the process, the metal oxide (Me_xO_y) reacts with the fuel, producing CO_2 and water (equation 1). Water can then be removed by condensation. The reduced metal oxide (Me_xO_{y-1}) is transferred to a separate reactor, where it receives oxygen from air and is re-oxidised (equation 2). The re-oxidised metal oxide is then returned to the fuel reactor for reuse, forming a continuous chemical-looping process. CLC was first proposed in the 1950s as a method to produce high-purity CO_2 from a hydrocarbon fuel source.

Reaction between fuel and metal oxide:



Oxidation of reduced metal oxide:



Most early research has focused on CLC applied to gaseous fuels. There are inherent challenges when applying this technology to solid fuels. When heated, solid fuels will release volatiles, which will react with the oxygen carrier to form CO_2 and H_2O . The remaining char typically requires gasification for complete conversion.

A closely related process to chemical looping is chemical looping with oxygen uncoupling (CLOU). Here the OC releases the oxygen in the fuel reactor. Thus, instead of the fuel reacting directly with the oxide, the oxidation of the fuel occurs in two stages: first, the release of the gaseous oxygen, and then the combustion of the fuel by the released O_2 . This process can allow for higher conversion of solid fuels, which can be challenging to combust in CLC processes. The CLOU process requires an OC with the ability to react with oxygen in the air reactor, but that decomposes to a reduced metal oxide and gas-phase oxygen in the fuel reactor. Three monometallic oxide systems with desirable thermodynamic properties have been identified: Mn_2O_3/Mn_3O_4 , CuO/Cu_2O and Co_3O_4/CoO . Co_3O_4/CoO has the disadvantage of an overall endothermic reaction in the fuel reactor, as well as high costs and health and safety considerations. For Mn_2O_3/Mn_3O_4 , temperatures below around $800\text{ }^\circ\text{C}$ are required in the air reactor. Reaction rates at these temperatures, however, appear to be too slow for successful operation. CLOU using CuO has been shown to work, and has been evaluated at 50-kW_{th} scale (Lyngfelt and Linderholm 2017). The oxidation reaction occurring with Cu_2O is outlined in equation 3:



At high temperatures, the equilibrium of the metal oxidation reaction favours Cu_2O . The equilibrium partial pressure of O_2 is about 0.05 atm at $950\text{ }^\circ\text{C}$ for CuO/Cu_2O . The air reactor has a high oxygen concentration; thus, equation 3 progresses to the right. In the fuel reactor, the O_2 concentration is low, thus the reverse of reaction 3 occurs, releasing O_2 .

As with oxyfuel combustion, CLC produces a highly concentrated CO_2 product stream. Thus, the techniques used to purify the CO_2 product stream from oxyfuel combustion can also be applied to CLC. In some instances, unreacted fuel can remain in the CO_2 product stream. When this happens, a final O_2 polishing stage of the product gas is required.

CLC processes typically operate in the temperature range $700\text{--}1000\text{ }^\circ\text{C}$. These temperatures are high enough to generate steam for power production, but low enough that formation of NO_x

pollutants is significantly reduced. Additional advantages of CLC include the high-purity CO₂ stream produced, and the lack of a requirement for a separate ASU, significantly reducing the capital costs of the process (however, this may still be required if an O₂ polishing step is used). Challenges include reducing the cost of the OCs used, and minimising replacement requirements due to attrition, loss of reactivity and agglomeration. In addition, carryover of unreacted carbon to the air reactor can reduce CO₂-capture efficiencies. To avoid this, a carbon separator can be used upstream of the air reactor.

Significant laboratory-scale research is still being conducted evaluating OCs, particularly low-cost carriers, for CLC processes. Significant research and development has been undertaken at Chalmers University, more recently focusing on scale-up challenges (SUCCESS 2018), and the potential for negative CO₂ emissions through CLC of biomass (Moldenhauer et al. 2019, Chalmers 2019). The Korean Energy Research Institute noted that at temperatures above 900 °C, fuel conversion and CO₂ selectivity of NiO-based OCs decreased with increasing temperature, due to the incremental formation of CO. They evaluated several metal oxides for improving fuel conversion in the high-temperature range, and found most benefit when adding Co₃O₄ to the OC (Ryu et al. 2017). Because of their low cost and good environmental aspects, Mn-based OCs are being considered. CSIC have evaluated several Mn-based OCs for use with gaseous fuels. Results showed that an OC impregnated using ZrO₂ as support had high reactivity and low attrition rate (Costa et al. 2017). The University of North Dakota are evaluating methods for addressing some of the challenges associated with CLC, such as high cost and loss of OC, and reduced carbon-capture efficiency due to carbon slip. To minimise carbon slip, they are evaluating a spouted fluidised-bed reactor design. To minimise cost, they are developing low-cost engineered OCs, and also evaluating the potential for recycling fines lost due to attrition (Nasah 2018). The University of Utah has been conducting research evaluating Si-supported Cu/CuO for CLOU. Their recent collaboration with Amaron Energy has scaled up production of the carrier to 100 kg batches. They are currently commissioning a 200-kW_{th} pilot-scale reactor for evaluating the CLOU process (Whitty 2018). CSIRO have recently commissioned a bench-scale CLC process using ilmenite as the OC for CLC with Victorian brown coal (Yamaguchi et al. 2018).

In-situ gasification CLC (iG-CLC) indicates a solid-fuel-based CLC process where no CLOU takes place. The University of Kentucky Centre for Applied Energy Research has used Fe-based carriers for an iG-CLC process. For larger-scale evaluation they used a fluidised-bed reactor (0.43 m diameter, 0.75 m high). A 3-kW electric oven was used to maintain uniform bed temperatures (Chen et al. 2016). In a recent DOE-funded study, the University is developing an advanced, coal-fuelled, pressurised CLC technology. The fluidised-bed reactor has been modified to a novel, spouted bed to avoid OC agglomeration, improve plant efficiency and reduce process complexity. Operating under elevated pressure is expected to improve the gasification rate of solid fuels, and reduce vessel sizes and solids inventory, thereby reducing capital costs. The system will also produce a high-pressure CO₂ stream, reducing energy requirements for downstream CO₂ compression (Chen et al. 2017, Liu et al. 2018). What remains is the challenge to demonstrate long term operation of high pressure interconnected fluidized bed reactors with very different gas atmospheres upstream of turbomachinery.

An alternative to the traditionally employed inter-connected fluidised bed reactors is to use dynamically operated packed bed reactors (Noorman et al. 2007, Hamers et al. 2013). This avoids the challenges of gas-solids separation and loop sealing experienced by fluidised bed systems when

operated at high pressure. This was evaluated for use with syngas as part of the DemoCLOCK project. This concept was demonstrated on a 10 kW standalone packed bed using ilmenite as the oxygen carrier (Gallucci et al. 2015). A preliminary techno-economic assessment suggests CO₂ avoidance costs comparable to a supercritical power plant with CCS. Relative to an unabated IGCC plant, the CO₂ avoided cost was found to be €34/tCO₂ (compared to €47/tCO₂ avoided for and IGCC power plant with pre-combustion CO₂ capture) (Mancuso et al. 2017).

Lyngfelt and Linderholm (2017) provided an overview of CLC research completed at pilot scale over the last 14 years. This is reproduced in Table 23 and provides a snapshot of the current level of demonstration achieved. A few companies and research organisations are now progressing the development of specific CLC technologies. An overview of these is provided in Table 24.

Table 23 Pilot-scale chemical-looping combustion operation (reproduced from Lyngfelt and Linderholm 2017)

LOCATION	SCALE [KW _{TH}]	FUEL TYPE	OXIDES EVALUATED	YEAR
Chalmers	10	Natural gas, oil	NiO, Fe ₂ O ₃ , CaMnO ₃ , ilmenite	2004
Korea Institute of Energy Research (KIER)	50	Natural gas	NiO, CoO	2004
Spanish National Research Council (CSIC)	10	Natural gas	CuO, NiO	2006
Chalmers	0.3	Natural gas, syngas	NiO, Mn ₃ O ₄ , Fe ₂ O ₃ , CuO, ilmenite, CaMnO ₃ , Mn/Fe, Mn/Mg, Mn/Si, Mn/Fe/Si, Mn ore	2006
Chalmers	10	Coal, petcoke	Ilmenite, manganese ore	2008
CSIC	0.5	Natural gas, acid gas, sour gas, ethanol	CuO, NiO, Fe ₂ O ₃ , CaMnO ₃	2009
King Abdullah University of Science and Technology	1	Methane	NiO+Fe ₂ O ₃	2009
Vienna University of Technology	140	Natural gas	Ilmenite, NiO, CuO	2009
Alstom	15	Natural gas	NiO	2009
Nanjing	10	Coal, biomass	NiO, Fe ₂ O ₃	2009
KIER	50	Natural gas, syngas	NiO, CoO	2010
Nanjing	1	Coal, biomass, sewage sludge	Fe ₂ O ₃ (ore)	2010
IFP-Lyon	10	Methane, coal, syngas	NiO, CuO, Mn ore	2010
Stuttgart	10	Syngas	Ilmenite	2010
Xi'an Jiaotong	10	Coke oven gas	CuO/Fe ₂ O ₃	2010
CSIC	1.5	Coal	Ilmenite, CuO, Fe ₂ O ₃	2011
Chalmers	0.3	Kerosene	NiO, Mn ₃ O ₄ , CuO	2011
Chalmers	100	Coal, petcoke, wood char	Ilmenite, Fe ore, Mn ore	2012
Hamburg	25	Coal	Ilmenite	2012
Ohio	25	Coal	Fe ₂ O ₃	2012

LOCATION	SCALE [KW _{TH}]	FUEL TYPE	OXIDES EVALUATED	YEAR
Nanjing	50	Coal	Fe ore	2012
Tsinghua	0.2	CO	Ilmenite	2013
Alstom	3000	Coal	CaSO ₄ /CaS	2014
CSIC	50	Coal, lignite, anthracite	Ilmenite, Fe ore, CuO/Fe ₂ O ₃ /MgAl ₂ O ₄	2014
Darmstadt	1000	Coal	Ilmenite	2015
Huazhong	5	Methane, coal	Fe ore	2015
Guangzhou	10	Saw dust	Fe ₂ O ₃	2015
Nanjing	25	Rice husk	NiO, Fe ore	2015
KIER	200	Natural gas	NiO	2016
Huazong	5	Coal	Fe ore	2016
SINTEF	150	Methane	CuO	2016
Technical Research Centre of Finland	20	Biomass	Ilmenite	2016
National Energy Technology Laboratory	50	Methane	CuO/Fe ₂ O ₃	2016
Chalmers	1400/1000	Biomass	Ilmenite, Mn ore	2016

Table 24 Summary of chemical-looping combustion research

TECHNOLOGY COMPANY/RESEARCH INSTITUTE	DESCRIPTION	COST AND ENERGY INFORMATION	REFERENCES
Coal direct chemical-looping combustion (CDCL) Ohio State University Babcock and Wilcox	Developed by Ohio State University. Uses Fe-based O ₂ carrier. Coal and CO ₂ are fed to the mid-section of the reactor. Char gasification occurs in the bottom section, with volatile combustion occurs in the upper section. Initial work on a 25-kW _{th} sub-pilot facility 250-kW _{th} facility constructed in 2015. 200 operating hours achieved. Current DOE-funded project is to complete a pre-front-end engineering design study for a 10-MW _e facility.	Preliminary techno-economic assessment suggests cost of electricity 102.67 \$/MWh (c.f. \$80.96/MWh for base plant, \$132.56/MWh for MEA). Net plant efficiency 35.6% (c.f. 39.3% base plant, 28.5% MEA).	Velazquez-Vargas 2017 Velazquez-Vargas et al. 2018
Limestone chemical-looping system Alstom	Has the potential for combustion with CO ₂ capture, gasification with syngas production or using carbonate loop for H ₂ production. 100-kW _{th} test facility. 3-MW _{th} pilot plant. Autothermal operation achieved with coal feed. <5% unburned C, 96% CO ₂ -capture efficiency.		Levasseur 2016

The EU project, SUCCESS, focused on providing information needed for scale-up of CLC applied to gaseous fuel. This included providing information on operating challenges through pilot-scale evaluation and also scale-up of OC manufacture. During the project, 100 kg batches of two different OCs were achieved from readily available raw materials. The project also evaluated commercially

available Al_2O_3 support materials for a CuO-based carrier. Several pilot-scale operations were achieved (10–1000 kW_{th}) to evaluate the process (SUCCESS, 2018).

Discussion on commercialisation potential and development since previous review

While techno-economic evaluations for CLC systems have been performed (e.g. in the EU ENCAP and ECLAIR projects), little information relating to the design and cost estimations for the CLC boilers has been published (Lyngfelt and Leckner 2015).

Mantripragada and Edwards (2017) evaluated the economics of using a chemical-looping process for an integrated gasification combined-cycle (IGCC) power plant. Costs for the air and fuel reactors were extrapolated from the costs of fluidised-bed biomass gasifiers of similar design to the CLC reactors. They found that the chemical-looping technology resulted in lower overall plant energy penalties compared with CO_2 capture via standard technologies (water–gas shift (WGS) plus Selexol). However, the chemical-looping process was found to be more capital intensive, leading to the overall cost of the chemical-looping plant to be greater than or similar to the conventional technologies. Cost of CO_2 avoided for CLC was in the range \$50–52/ tCO_2 compared with \$54.5/ tCO_2 for the Selexol-based process. LCOE was \sim \$142/MWh for the CLC process compared with \$141/MWh for the Selexol-based process.

Lyngfelt and Leckner (2015) compared the design of a CLC CFB to standard CFB technology and used this to provide an estimate of the cost of a CLC process. They note that while the design of the circulating reactors in CLC systems will be largely similar to CFB boilers, some alterations will likely be required due to differences in bed material, insulation, and strategies for introducing fuel and air to the reactors. They estimate the cost of CLC with capture relative to CFB without capture to be 20 €/t CO_2 . The largest cost was associated with the compression of the CO_2 . Interestingly, the second-highest cost was the need for a small ASU to provide oxygen for the polishing step.

While NiO has been widely used for CLC in early research, in their evaluation, Mantripragada and Rubin (2017) found that despite the lower oxygen-carrying capacity of an iron-based OC, its lower cost meant that the full plant cost was only slightly above that of the NiO-based OC. They note the added disadvantage that Ni-based compounds have adverse health effects, requiring special care in design to prevent any releases. Lyngfelt and Linderholm (2017) state that for solid-fuel-based CLC, the use of NiO can be excluded due to its high cost, toxicity and incompatibility with sulfur.

The air and fuel reactors in a CLC process are interconnected fluidised beds, with the OC as the circulating bed material. The process temperature for CLC is comparable to conventional combustion processes; thus, the CLC reactor system can be used in the same way as a conventional CFB in a steam-cycle process.

As mentioned above, significant pilot-scale evaluation has been achieved, particularly for gaseous fuels. Most of this, however, has been at scales $<200 \text{ kW}_{\text{th}}$. Recently, 1-MW $_{\text{th}}$ pilot-scale evaluation has been undertaken. However, challenges still exist. Lyngfelt and Linderholm (2017) noted that during operation with coal, the 1-MW $_{\text{th}}$ facility suffered from large loss of carbon from the fuel reactor, either to the air reactor (for larger coal particle sizes) or elutriated (for smaller coal particle sizes). The significant pilot-scale operation is a clear indication of advancement of CLC processes. In the previous IEAGHG review, issues observed during pilot-scale operation around lack of complete combustion (volatile release, unburned C) led to the technology being assessed at a TRL of 2. Integrated gasification CLC was assessed as being at the concept stage, and thus a TRL of 1.

CLOU was similarly assessed as being at a TRL of 1. Ohio University's Coal direct chemical-looping concept was similarly assessed as being at TRL of 1. Due to evaluation on its 3-MWth pilot plant, Alstom's limestone chemical-looping process was evaluated as being at a TRL of 4. Since then, further pilot-scale evaluation has certainly been achieved, processing several fuel types. While C loss can still be an issue, methods for dealing with this (O₂ polisher, C removal step) have now been demonstrated. The CLC process is intended to replace standard power-generation technology. This makes it slightly different from conventional capture technologies, for which electricity production is achieved in a separate plant. To date, CLC incorporating power production has not been demonstrated. In addition, long-duration evaluation (around 1000 h) has only recently been achieved at pilot scale. For these reasons, the technology is assessed as being at a TRL of 4–5.

Scale-up of CLC processes will be able to take advantage from development of CFB combustion systems. While the design of the circulating reactors in CLC systems will be largely similar to CFB boilers, Lyngfelt and Leckner (2015) note that some alterations will likely be required due to differences in bed material, large increase in solid circulation rates, and strategies for introducing fuel and air to the reactors.

4 Oxyfuel combustion technologies

Section 4 discusses advances in oxyfuel combustion, air separation, and CO₂ purification and flue-gas treatment.

In oxyfuel processes, nitrogen is removed from the air prior to combustion, as outlined in Figure 11. The carbonaceous fuel is then burned in nearly pure oxygen (typically 95–97%), producing a flue gas consisting mainly of CO₂ and water (Stanger et al. 2015). Some oxyfuel technologies, such as NET Power’s Allam cycle, require very high purity oxygen (99.5%) (Stanger et al. 2015). When fuel is burned in pure oxygen, the flame temperature is excessively high, so a portion of the CO₂ (and H₂O)-rich flue gas can be recycled to the combustor to reduce the flame temperature. Recycled flue gas is also required to provide sufficient volume to carry heat into the convective pass of the boiler (for systems modified from air-firing). Typically 65–75% of the flue gas from the boiler is recycled (Stanger et al. 2015). The remainder of the CO₂ is then available for subsequent storage or utilisation. The produced CO₂ still contains water vapour, impurities (particularly some SO_x and NO_x) and incondensable components, such as O₂, N₂ and Ar from the ASU and also from air leakage. The concentration of CO₂ produced from oxyfuel combustion is typically around 60–75% wet (Lockwood, 2014; Kanniche et al. 2010).

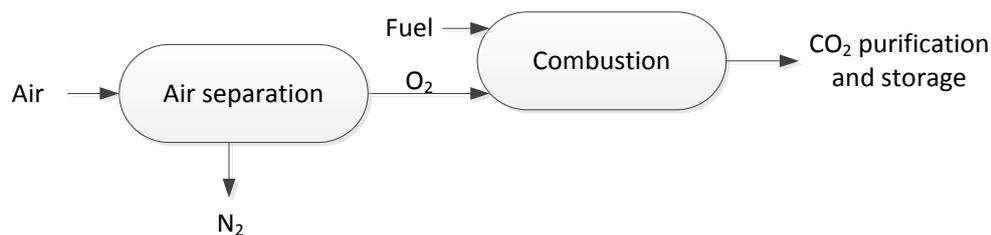


Figure 11 Oxyfuel combustion process

The flue gas will typically pass through particulate removal and FGD, similar to standard combustion processes. A flue-gas cooler is also used to remove the bulk of the water (around 80%). A CPU removes final impurities from the CO₂-rich flue gas and compresses the CO₂ for transportation. The cost of the CPU is around 7–10% of the total plant cost, depending on the number of purification steps required. The level of purification applied depends on the final use of the CO₂. For pipeline specifications, water should be removed to low levels. This necessitates flue gas drying beyond the simple condensation achieved in the flue gas cooler. If the CO₂ is to be used for EOR, O₂ concentrations below 14 ppm are required (Lockwood 2014).

Removal of acid gases (SO_x and NO_x) can be achieved by several processes, including conventional alkaline scrubs, pressure-swing adsorption, distillation of NO₂, and a novel sour compression process (Lockwood 2014). Flue-gas drying is typically achieved via temperature swing adsorption. Separation of CO₂ from the inert gases and oxygen is carried out by a partial condensation of the process gas at cryogenic temperatures. This involves both an initial compression step and cooling to temperatures approaching the triple point of CO₂. The heavily insulated container in which all low-temperature processes occur is referred to as the cold box. The CO₂-rich liquid obtained can then be further purified by flash separation (CO₂ for storage) and distillation steps (higher purity for EOR). Each of these purification processes has the potential for CO₂ losses; however, the majority are noted to be

from 'vent gases' released from the cold-box processes. Some designs include additional extraction of CO₂ remaining in these vent gases, with calculations suggesting capture rates of around 90% could be increased up to 98% (Lockwood 2014). Manufacturers have employed either membrane-based systems or PSA for this purpose.

Both cryogenic air separation and the final CO₂-purification technologies are already well established. They are, however, energy intensive. As such, ongoing research tends to focus on reducing the energy consumption of the process. Large pilot-scale (30 MW_e) operation of the oxyfuel process has been achieved at Callide power station in Australia. Oxyfuel plants are generally estimated to offer similar capture costs to standard PCC processes (IEAGHG 2014b, Wood 2018). Several oxyfuel demonstration plants reached advanced stages of planning, but were cancelled prior to construction (Lockwood 2016).

The three main steps in an oxyfuel process include air separation, combustion, and final CO₂ compression and purification. Research into improvements related to oxyfuel combustion have tended to focus on these three categories.

4.1 Advances in oxyfuel combustion

4.1.1 Pressurised solid fuel oxyfuel combustion

Efficiency gains and cost reductions can potentially be achieved if the oxyfuel process is operated at higher pressures. Pressurisation avoids air ingress to the process, and the penalty associated with pressurising O₂ is offset by reduced compression requirements for the CO₂ product. A pressurised system will require thicker walls and other features, such as gas tight seals, which will increase cost. However, the higher pressure reduces the volume of flue gas being treated, and therefore also the equipment size. The water vapour present in the flue gases can be condensed at higher temperatures, and thus the latent heat of condensation can be used to improve overall cycle efficiency (Lockwood 2016, Gopan et al. 2014). The combined energy gains are estimated to provide 3–5% absolute efficiency advantage over an atmospheric oxyfuel boiler (Lockwood 2016). Soundarajan and Gundersen (2013) compared the performance of pressurised oxyfuel with an atmospheric counterpart. They determined an efficiency improvement of 1.7 percentage points for the pressurised boiler. Hong et al. (2010) completed a sensitivity analysis on the effect of combustor pressure and found the maximum efficiency was achieved at around 10 bar. Reaction Engineering International in collaboration with the University of Utah, Praxair and Jupiter Oxygen Corporation are performing multi-scale experiments, coupled with mechanism development and computational fluid dynamics modelling to generate tools and mechanisms that are capable of describing high temperature and pressurised oxycoal combustion (Chido 2017). Pressurised oxyfuel combustion has been studied by several researchers (Hong et al. 2009, Zebian et al. 2012, Ying et al. 2016). Three technologies in particular are being progressed and have achieved pilot-scale demonstration. These are summarised in Table 25. A flow diagram of the staged pressurised oxyfuel combustion process is provided in Figure 12.

Table 25 Pressurised oxyfuel combustion technologies that have reached pilot-scale evaluation

TECHNOLOGY COMPANY/RESEARCH INSTITUTE	DESCRIPTION	COST AND ENERGY INFORMATION	REFERENCES
ITEA flameless technology Unity Power Alliance (joint venture between ITEA and ThermoEnergy corp.)	<p>Isothermal flameless oxyfuel combustion. Coal slurry fed to refractory-lined reactor operating at 10 bar. Combusted with pressurised mix of O₂ and recycled flue gases. Due to water addition, only around 20% flue-gas recycle required for temperature control. The resulting combustion is flameless (1400–1700 °C). Flue gases are recycled hot, and thus combustion chamber is maintained at uniform hot temperature. Non-recycled flue gases quenched to 800 °C prior to steam generator and condensing heat exchanger. This exchanger is the main means of heat transfer to boiler feedwater, and a large amount of recycle is required to increase flow through the HX to aid heat transfer.</p> <p>Evaluated at 5-MW_{th} facility operating at 4–6 bar. 15-MW_{th} waste incinerator in Singapore operated in flameless mode for 2 years.</p> <p>100-kW_{th} demonstration facility built with support from DOE. Operated at pressures of 15 and 32 bar. Simulation suggests optimum efficiency at 29 bar.</p> <p>Recent DOE-funded study preparing design for a 50-MW_{th} facility.</p>	<p>Simulation suggests 33% efficiency achievable (higher heating value), 5% points above atmospheric oxyfuel combustion.</p> <p>Techno-economic analysis suggests first-year cost of electricity (COE) \$86/MWh, cost of CO₂ avoided \$37/tCO₂.</p>	<p>Lockwood 2014 Malavasi and Landegger 2014 Reineck 2017</p>
Stage-pressurised oxyfuel combustion (SPOC) Washington University in St Louis	<p>Pressurised oxyfuel combustion with minimal CO₂ recycle. This is achieved by using consecutive (typically 4) pressurised combustion chambers and staging the addition of fuel. In the first combustion stage there is sufficient excess O₂ to limit the combustion temperature. Additional fuel is then added in subsequent combustion stages. Radiative heat exchangers are used to raise steam and limit flue-gas temperatures. By using O₂ and prior stage combustion products as diluent gases, the proportion of flue-gas recycle required can be significantly reduced. Simulation has shown that efficiency drops with increase in fuel moisture content, and hence slurry feeding is not recommended.</p> <p>100-kW test reactor has achieved 200 h of operation. Achieved improved system reliability and burner design.</p> <p>Department of Energy (DOE) is currently funding further development of this technology with a project demonstrating integrated pollution removal with simultaneous heat recovery.</p>	<p>Simulation of 550-MW plant showed 6% point reduction in energy penalty compared with conventional oxyfuel (from 29.3% for conventional oxyfuel, to 36.7% HHV for SPOC).</p> <p>Levelised COE for SPOC process \$98.5/MWh (c.f. \$73.05/MWh for baseline air-fired plant without carbon capture).</p>	<p>Axelbaum et al. 2017 Gopan et al. 2014</p>

TECHNOLOGY COMPANY/RESEARCH INSTITUTE	DESCRIPTION	COST AND ENERGY INFORMATION	REFERENCES
Pressurised fluidised-bed combustion GTI (formerly Aerojet Rocketdyne)	<p>Uses an in-bed heat exchanger to achieve an ultra-compact combustor (1/3 size and 1/2 cost of traditional boiler). Fluidised bed allows for fuel flexibility. Limestone injection used for SO₂ removal. Current program focused on oxy-PFBC with steam Rankine cycle. Added efficiency expected if supercritical CO₂ Brayton cycle used.</p> <p>Primary contributors to lower cost include reduced capital expenditure from lower-cost combustor and gas clean-up equipment.</p> <p>DOE is currently funding further development of this technology through an ongoing experimental campaign using the 1-MW_{th} pilot plant.</p>	<p>Preliminary economic analysis with steam Rankine cycle suggests COE increase of 30% (compared with DOE case 11) with capture cost <\$30/t. This is expected to decrease to 18% increase in COE with supercritical CO₂ Brayton cycle.</p> <p>The current GTI Oxy-PFBC baseline design is predicted to achieve a COE decrease of 22% with 98% CO₂ capture compared with a pulverised coal plant with post-combustion capture.</p>	<p>Follett 2017 Follett 2016</p>

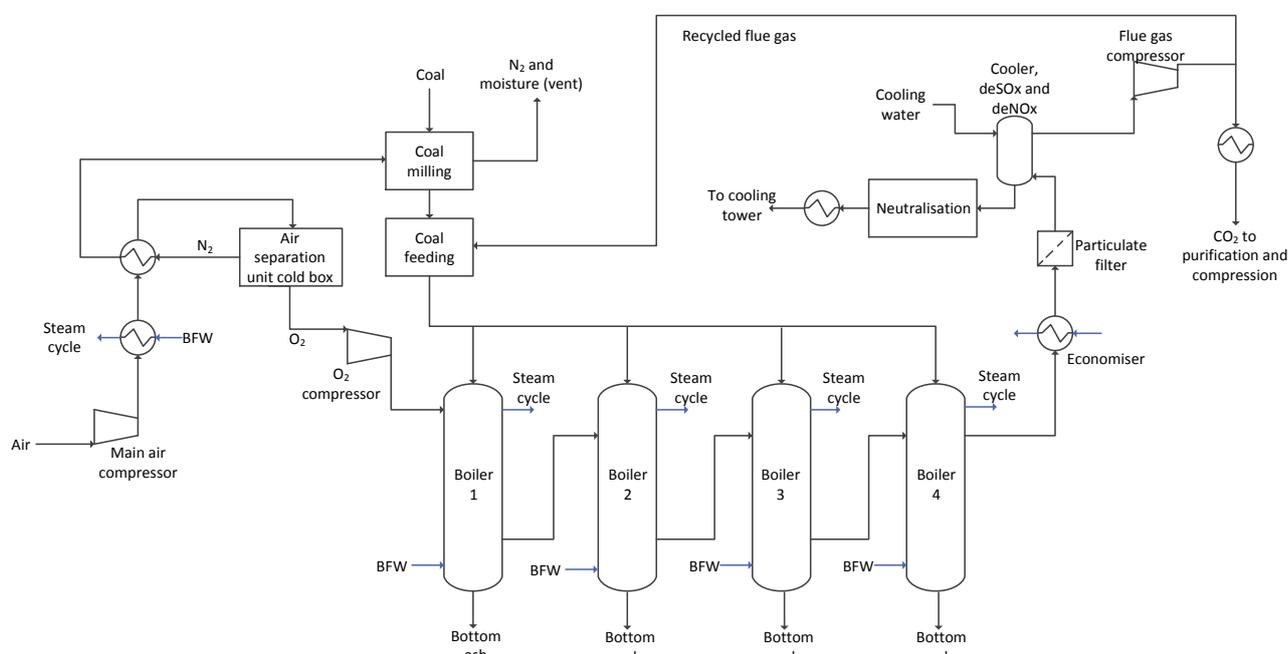


Figure 12 Flow diagram of staged pressurised oxyfuel combustion process (Gopan et al. 2015)

More recent research work has focused on developing systems other than the combustor/boiler that would be required for pressurised oxycombustion. GTI have developed a transport membrane condenser, latent-heat and water-recovery technology that extracts water vapour from flue gases. This nanoporous, ceramic-separation membrane was commercialised for use with gas-fired industrial boilers in 2009. In a recent DOE-funded project, this technology is being adapted for use with pressurised coal oxycombustion boilers. Water vapour in the flue condenses and passes through the membrane, producing high-purity water, and the associated latent heat of condensation can be directly added to the boiler feedwater stream. Contaminants and permanent gas components, such as CO₂, O₂, NO_x and SO_x are inhibited from passing through the membrane by its high selectivity. The improved transfer of heat to the steam condensate results in higher efficiency. The system is to be evaluated at GTI's pilot-scale, fluidised-bed coal gasifier/combustor (Wang 2017). To further develop the staged pressurised oxyfuel combustion (SPOC) process, Washington University in St Louis is undertaking a DOE-funded project to investigate integrated

pollution removal with latent heat recovery from the flue gas stream. A prototype test device is to be constructed and integrated with their 100-kW_{th} pilot combustion facility. The combined removal of SO_x and NO_x components is expected to minimise equipment needs and hence reduce costs. Techno-economic studies suggest incorporating the integrated pollution-removal process with SPOC increases the efficiency of the oxycombustion cycle by more than 6 percentage points above first-generation oxycombustion processes (Axelbaum 2017). To further develop the pressurised fluidised-bed combustion system, GTI is undertaking additional experimental campaigns using the CanmetENERGY 1-MW_{th} pilot plant. The technologies being developed include: in-bed supercritical CO₂ heat exchanger, staged coal combustion, and an isothermal deoxidation reactor (Fitzsimmons 2017).

Discussion on commercialisation potential and development since previous review

Of the advances in pressurised oxyfuel combustion, the Unity Power Alliance, University of Washington and GTI programs are the most advanced. Despite facing challenges with the scaled-down 100-kW_{th} facility, the Unity Power Alliance IsoTherm process has achieved a TRL of 5 with the operation of the 5-MW_{th} facility in Italy and 15-MW_{th} facility in Singapore. The ongoing DOE project building a 50-MW_{th} facility will increase the TRL. Techno-economic analysis of the process has produced mixed results, with some suggesting the benefits of the IsoTherm process are not significantly better than an optimised atmospheric oxyfuel combustor (Hagi et al. 2014). The large amount of flue-gas recycle required appears to be the largest contributor to this reduced efficiency.

For the SPOC process, the DOE-funded development undertaken by the University of Washington and Electric Power Research Institute (EPRI) has evaluated this technology as having reached a TRL of 5. In their analysis, Hagi et al. (2014) raised concerns regarding the capability of the process to handle the radiative heat transfer, especially when ultra-supercritical steam conditions are considered. In the project final report, additional data were required to validate computational fluid dynamics sub-models, which had not previously been applied to conditions of high pressure or high O₂ concentrations. Further experiments were being undertaken on the 100-kW_{th} facility to generate this data. This technology is being further progressed with additional DOE funding, evaluating additional components of the overall process such as the integrated pollution control with heat recovery. Input is also being sought from OEM boiler manufacturers for input on steam-cycle integration, boiler-tube surface arrangement and operational flexibility.

The GTI process is currently being progressed to a TRL of 6 through the 1-MW_{th} pilot operating in Canada. In addition, long life in-bed heat exchangers, as used in the process, have been demonstrated since the 1980s.

The previous review discussed pressurised oxyfuel combustion technologies, but did not elaborate on their TRLs. Since the previous review, the ITEA, SPOC and GTI technologies have progressed to further pilot-scale demonstration. Full system integration has not yet been demonstrated, and this appears to be the focus of ongoing, pilot-scale demonstration work. This suggests the technologies have reached a TRL of 5, with current demonstration work progressing them to a TRL of 6.

4.1.2 Other oxyfuel combustion research

Some additional research has been conducted investigating modifications to the combustion process of an oxyfuel plant. The Jupiter Oxygen Corporation evaluated a high-flame temperature process. This was originally developed for use in aluminium-melting furnaces. Fuel and O₂ are mixed undiluted, leading to high flame temperatures (>2400 °C) and enhanced heat transfer in the radiant zone of the boiler. A DOE-sponsored project evaluated the technology for utility power-plant applications. A 15-MW_{th} pilot test facility was constructed and operated through to 2012. Preliminary economic projections suggest 95–100% CO₂ capture can be achieved with cost of electricity (COE) increase <35% for a CO₂ cost of \$20/t (Schoenfeld et al. 2012).

GTI evaluated a pressurised molten bed oxycoal boiler, in which coal and O₂ are charged directly to a pressurised molten slag bed boiler. The slag transfers heat directly to steam tubes in the walls that are protected by a thin layer of refractory and frozen slag. As the slag redistributes the combustion heat, minimal flue-gas recycle is required. The technology builds on the proven technologies of submerged combustion melting and evaporative cooling. A preliminary techno-economic assessment calculated an overall plant efficiency, including CO₂ compression, of 31.6% (first-generation oxyfuel plant efficiency 29.2%). COE was calculated to be 34% higher than the COE for a standard air-coal supercritical steam power plant with no CO₂ capture. The economic analysis was completed as part of a DOE-sponsored project. Phase 2 of the project was not continued (Rue 2013).

The Technical University of Munich evaluated controlled staging with non-stoichiometric burners, aiming to reduce the flue-gas recirculation required to maintain flame temperatures. The concept was evaluated in a 3 x 70-kW natural-gas-combustion test rig. Flue-gas recirculation was reduced from 70 to 50%. Increased heat flux due to increased radiation was also noted with the decrease in flue-gas recycle (Becher et al. 2011).

O2GEN (Optimisation of Oxygen-based CFBC Technology with CO₂ capture) was an EU-funded project under the FP7 framework that was finalised in 2016. Optimisation of the oxyfuel CFBC process was particularly focused on using higher O₂ concentrations in the furnace. A 100-kW_{th} pilot-scale evaluation was completed with 40% O₂ at the Technical Research Centre of Finland. This was followed by larger CFB combustion tests carried out by CIUDEN (Spain's Fundación Ciudad de la Energía). During the two-week evaluation at CIUDEN, no significant operational problems were encountered. SO₂-capture efficiency was found to be similar to standard oxycombustion conditions, and NO_x emissions were noted to increase with increasing boiler load, bed temperature and primary oxidant share. Improvements in the ASU and CPU were seen, and heat integration was also optimised for the process, with the efficiency penalty estimated to reduce from 10.5 to 7.3 percentage points (Espatolero and Romeo 2017, Pikkarainen et al. 2014). A summary of additional oxyfuel combustion technologies being evaluated is provided in Table 26.

Table 26 Summary of other oxyfuel combustion research

TECHNOLOGY COMPANY/RESEARCH INSTITUTE	DESCRIPTION	COST AND ENERGY INFORMATION	REFERENCES
Pulse-detonation engine Oregon State University	Evaluating a pulse-detonation combustion system for direct power extraction. Controlled detonations of fuel and air/O ₂ produce high-speed shockwave of high pressure and temperature (>3000K). The fluid generated can be used in a magnetohydrodynamic generator (MHD) to generate power. The resulting flue gases can then be used in a traditional steam cycle for additional power generation. The current DOE sponsored project is designing a prototype unit to operate on gaseous or solid fuels.	By using high-temperature gases as a working fluid in a MHD topping unit, a combined-cycle coal-fired power plant is expected to achieve plant thermal efficiencies close to 60%.	Blunk et al. 2015
Novel combustor concepts University of Texas at El Paso	Developing novel combustor components that can be used in high-temperature energy systems, such as oxyfuel-based MHD systems. Existing combustion research facilities modified to accommodate high temperature and high velocity oxyfuel flow.		Love 2017
Moderate and intensive low oxygen dilution Project coordinated by SINTEF	Oxyfuel combustion investigated as part of the European BIGCO ₂ project. Intensive recirculation of hot combustion products allows fuel to combust in dilute O ₂ environment. Internal recirculation also thought to lower external flue-gas recirculation required to moderate combustion temperatures. Computational fluid dynamics simulation of full-scale boiler completed to optimise geometry.	Estimate 3% point increase in efficiency over conventional oxycombustion (from 33.5% for a standard oxyfuel system to ~37% for MILD, depending on operating conditions chosen).	Molnvik et al. 2012 Adamczyk et al. 2017

Some oxyfuel technologies achieve increased efficiency when paired with a supercritical CO₂ Brayton cycle. A recent DOE-funded project led by EPRI evaluated process designs for an oxy-fired PC, air-fired PC, and CLC power plant integrated with a closed Brayton power cycle. Comparison was made to DOE/NETL baseline cases employing steam Rankine cycles. While the Brayton cycles were found to be more efficient, the capital costs were also higher than the Rankine cycle equivalent case, leading to similar LCOE. The boiler/fired heater and power cycle costs in particular were significantly higher for the Brayton cycle cases (Maxson 2018).

To assist the development of fossil-fired supercritical CO₂ power plants, the DOE is also funding projects developing the high-temperature, high-pressure, heat exchangers required. Thar Energy is leading a project developing high-temperature, high-differential-pressure recuperator technologies suitable for use in sCO₂ recompression Brayton cycle (e.g. temperatures exceeding 700 °C and differential pressures in the order of 200 bar) (Chordia et al. 2015). Oregon State University, with support from Carnegie Mellon University, are developing low-pressure-drop designs for the high-temperature and high-pressure heat exchangers using microchannel architectures (Rasouli et al. 2016).

Discussion on commercialisation potential and development since previous review

Of technologies described above, most are at a very early stage of research. Only the Jupiter Oxygen Corporation high-flame temperature and the O₂GEN projects progressed to pilot-scale evaluation, but further development of these technologies do not appear to be ongoing. Thus, these technologies are assessed as having reached a TRL of 4–5. The magnetohydrodynamic concepts

appear to suggest significantly higher efficiencies than currently achieved with conventional steam cycles; however, this research is still at an early stage, with the first unit prototypes being developed. As such, these concepts as applied to oxycombustion are at a TRL of 1–2, with the potential to progress to 3–4 once the prototype units have been demonstrated.

4.1.3 Oxyfuel gas turbines

Oxyfuel combustion can be applied to combustion of natural or synthetic gas (produced via gasification of solid fuels) in high-temperature gas turbines. Several different cycles have been proposed, including the Allam cycle, Clean Energy Systems' cycle, water cycle, Advanced Zero Emission Power Plant, COOPERATE, MATIANT (semi-closed oxycombustion) and COOLENERG (Staicovici 2002). However, most of the development work to date has consisted of theoretical analysis and simulation. Only a few have progressed to larger experimental verification. A review of the more advanced process options is found in IEAGHG 2015/5 and IEA CCC/280. A short summary of the information provided on these technologies is provided in Table 27. A flow diagram of NET Power's Allam cycle is provided in Figure 13. For more detailed information, readers are referred to the aforementioned references.

The use of supercritical CO₂ (sCO₂) as the working fluid, as is the case with the Allam cycle, is gaining widespread interest. sCO₂ cycles were evaluated as far back as the 1960s, with the interest then being incorporation into nuclear power systems. Their potential for higher efficiencies and reduced capital are making them of interest again. Advanced sCO₂ power cycles offer many potential advantages, including high thermal efficiency, low capital cost, and 99% CO₂ capture. However, there is currently limited information on auto-ignition, combustion dynamics and flame dynamics in the region where sCO₂ oxycombustion power cycle combustors would operate.

The Georgia Institute of Technology is undertaking a DOE-sponsored project to measure auto-ignition delays of CO₂ diluted oxygen/fuel mixtures (natural gas and syngas) in a high-pressure shock tube (Sun et al. 2015). Unknowns for sCO₂ systems include material aspects (corrosion, creep, fatigue), turbomachinery (lifetime, aerodynamic performance, seals), recuperators (design, size, fabrication, durability) and cycle operability (Bush 2018). As a result, several test facilities have been developed. GTI, in collaboration with South West Research Institute and GE, are developing a 10-MW_e pilot sCO₂ facility. The Korean Institute of Energy Research operates two supercritical carbon dioxide power cycle experimental test loops (Cho et al. 2018). The University of Texas at El Paso are evaluating an oxyfuel high-pressure combustor (methane), designed to operate at up to a 250 kW power input and 20 bar pressure as part of a DOE-sponsored project (Chowdhury et al. 2018). In February 2018, DOE announced \$700K of funding to a team led by the University of North Dakota Energy and Environmental Research Centre for initial work on a coal-based Allam cycle pilot plant (Alley 2018).

Table 27 Oxyfuel gas turbines

TECHNOLOGY COMPANY/RESEARCH INSTITUTE	DESCRIPTION	COST AND ENERGY INFORMATION	REFERENCES
Trigen Clean Energy Systems (CES) cycle Maersk	<p>The CES water cycle adapts the combustor of a rocket engine to provide the main gas generator for the oxyfuel cycle. A steam-rich working fluid is generated (roughly 80% H₂O, 20% CO₂) which is used to drive a high-pressure steam turbine. The operating parameters of the first combustion chamber are temperatures between 1650 and 1750 °C, and pressures 50–100 bar. Water/steam injection used to moderate the temperature of the engine and produce a working fluid with gas temperature that matches the inlet temperature of downstream high-pressure (HP) steam turbine (500–700 °C). The working fluid exiting the HP turbine is reheated using external combustion to provide a temperature matching the inlet temperature of intermediate-pressure turbine. A final low-pressure steam turbine and condenser produces water for recycle and CO₂.</p> <p>The main combustor has been evaluated at 170-MW_{th} scale, and a Siemens SGT-900 gas turbine has been modified for use with the process, with inlet conditions of 16 bar and 967 °C. Development of a new turbine designed specifically for the process has been undertaken by Siemens. 200-MW_{th} HP combustor and 43-MW_e turbine have been operated.</p>	<p>A range of costs have been proposed for this process depending on the variant of the process used. In the IEAGHG study, the supercritical CES process was calculated to have an efficiency of 48.9% (LHV) and a levelised cost of electricity (LCOE) of 95.1 €/MWh.</p>	Lockwood 2016 IEAGHG 2015 Anderson et al. 2014
Allam cycle NET Power cycle 8 Rivers capital	<p>Supercritical CO₂ cycle where combustion products act as working fluid (recuperated Brayton cycle). The fluid at a pressure of 300 bar is heated to 1100–1200 °C by combustion using high-purity O₂. The hot gas is expanded to 30 bar in a turbine, dropping the temperature to 700 °C. The exhaust gases pass through a recuperating heat exchanger (HX), transferring heat to the inlet CO₂/O₂ fuel mix. Exhaust gases leaving the HX are further cooled and water removed. Some CO₂ product is removed (~5% of flow), with the remainder re-pressurised, reheated and recycled.</p> <p>50-MW_{th} pilot plant currently being commissioned in La Porte, Texas, in collaboration with Toshiba, Exelon and CB&I (Chicago Bridge & Iron Company, now merged with McDermott International). Toshiba are developing a new combustor and turbine for the process, using CO₂ as the cooling fluid and Ni alloy for portions of the inner casing and rotor. First fire of the facility was achieved in early 2018. A 300-MW_e commercial plant is currently in the design phase.</p> <p>The majority of the equipment used in the process is well established. Only the turbine and recuperating heat exchanger are at a lower TRL. Toshiba are developing the turbine used with the process, drawing on their knowledge of gas and steam turbines. Toshiba have operated a 5-MW_{th} combustion test unit, obtaining the required maximum test pressure (300 bar).</p> <p>The recuperating heat exchanger for the 50-MW_{th} pilot plant is being provided by Heatric.</p>	<p>In the IEAGHG report, the NET Power cycle had the lowest LCOE of technologies evaluated. Its LCOE was determined to be slightly lower than that of a conventional NGCC coupled with CO₂ capture via a proprietary liquid absorbent.</p> <p>The NET Power cycle was determined to have an efficiency of 55% (LHV) and a LCOE of 83.6 €/MWh in the IEAGHG study. The developers of the NET Power cycle have estimated an efficiency of 59% using proprietary improvements (51% for coal). The higher efficiency is expected to reduce the LCOE by 3–5 €/MWh.</p>	Carbon Capture Journal 2018 Allam et al. 2017 IEAGHG 2015 Rathi 2017 NET Power 2018

TECHNOLOGY COMPANY/RESEARCH INSTITUTE	DESCRIPTION	COST AND ENERGY INFORMATION	REFERENCES
S-Graz cycle University of Graz, Austria	<p>The Graz cycle essentially consists of a high-temperature Brayton cycle and a low-temperature Rankine cycle i.e. a high-temperature gas turbine (40 bar) followed by a heat-recovery steam generator (HRSG). Several modifications have been proposed. The working fluid is mostly steam, with some recycled CO₂.</p> <p>While many of the components used in the cycle are standard (HX, HRSG, low-pressure turbine), others still require development. These include the combustor, the high-temperature turbine (with CO₂/H₂O working fluid), and the condenser.</p> <p>More recently the Graz cycle has been evaluated for the combustion of H₂.</p>	The IEAGHG study evaluated the S-Graz process as having an efficiency of 49.2% (LHV) and a LCOE of 93.7 €/MWh.	IEAGHG 2015 Heitmeier et al. 2006 Sanz et al. 2005 Jericha et al. 2004 Jericha et al. 2008 Sanz et al. 2018
Semi closed oxycombustion combined-cycle (SCOC-CC)	Compressed gas is fired in a gas turbine with O ₂ and recycled flue gas generating electricity. Hot combustion products are used to generate steam for additional power generation. Although similar, it is not possible to retrofit a conventional gas turbine for oxyfiring due to the different physical properties of CO ₂ and air.	The IEAGHG study evaluated the SCOC-CC process as having an efficiency of 49.3% (LHV) and a LCOE of 92.8 €/MWh.	IEAGHG 2015

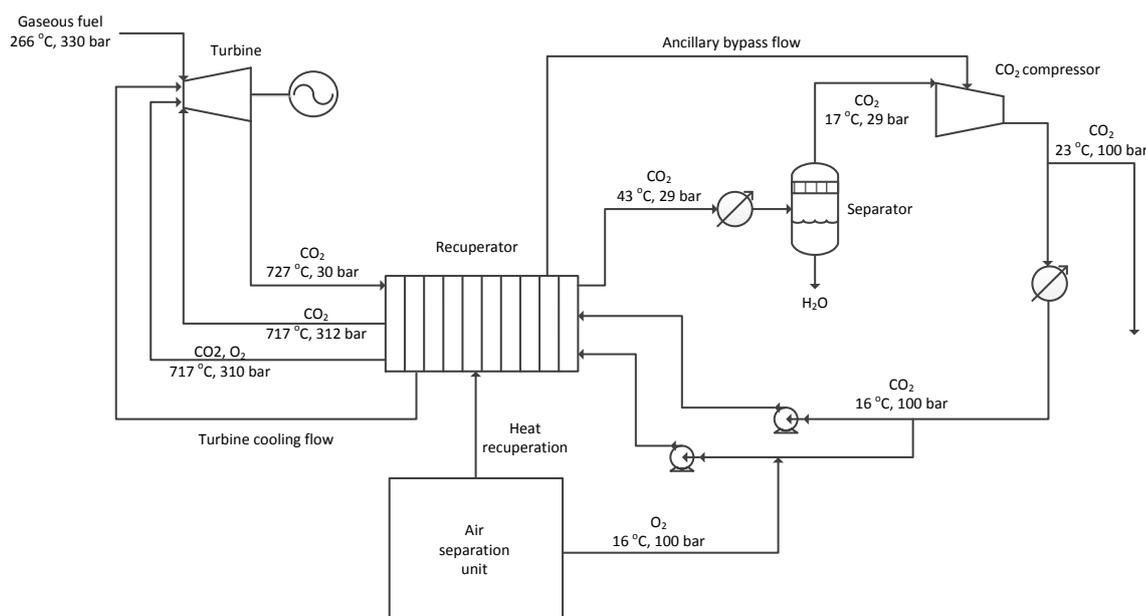


Figure 13 Flow diagram of NET Power's Allam cycle (Allam et al. 2017)

Discussion on commercialisation potential and development since previous review

While there are several theoretical studies on variations of oxyfuel gas turbines, only two are currently being progressed to an industrial scale by US-based companies, the NET Power Allam cycle and Clean Energy Systems' Trigen cycle. In the previous review, the majority of the alternative power cycles were assessed as being at a TRL of 2. The main exception was the process being developed by Clean Energy Systems, which was assessed at a TRL of 5. Since the previous review, the Clean Energy Systems' cycle has been further developed; however, the main development since then has been the progress of NET Power's Allam cycle.

Clean Energy Systems' Trigen cycle achieves competitive cycle efficiencies and cost of electricity if the intermediate-pressure turbine inlet temperature is in the range of 760–1250 °C. This is above

the capabilities of traditional steam turbines, but within the operational range of gas turbines. Thus, they have adapted a Siemens' gas turbine to work with a high-steam-content working fluid. This 150-MW_e expander turbine has been evaluated at their Kimberlina power plant. Some damage to the combustion liner was observed, but solutions have been determined. Further long-term testing is required; however, it is unclear whether further evaluation has taken place since that demonstration.

Further analysis of the Graz cycle has been undertaken, including evaluation of its use for H₂ combustion. The Graz cycle still requires the development of turbomachinery. Heitmeier et al. (2006) note that some combustor evaluation has been completed in Japan and by NETL, showing that oxyfuel firing using steam dilution is possible. The design of the high-temperature turbine has been evaluated at Graz University of Technology; however, experience is required for the behaviour of high-temperature alloys in the steam/CO₂ environment. The condenser has to deal with a large-volume flow due to the low pressure, and challenges with reduced heat transfer due to the presence of inert gas. Information is still required on heat transfer in this environment.

For the Allam cycle, the plant uses equipment already proven in industrial application, apart from the turbine, combustor and recuperating heat exchanger. By working with equipment manufacturers, the current commissioning of the 50-MW_{th} pilot plant will provide significant confidence in the full system. Toshiba in particular is completing the design and development of the turbine for both the current pilot plant and larger planned commercial plant. Toshiba has also successfully demonstrated a 5-MW_{th} combustor test unit.

Cost estimates for alternative oxycombustion power cycles are difficult to establish, as they require the development of new equipment. The work completed in the previous IEAGHG (2015) report, however, show significant advantages for the Allam cycle. At the recent GHGT-14 conference it was noted that 300 MW_e was selected for the size of the commercial plant, due declining industry interest in large, single power stations. In addition, at 300 MW_e the rotor for the Allam cycle is already 1 m in diameter. Larger sizes could require additional engineering. While smaller power plants are of interest, there will likely be a minimum practical size for the Allam cycle. This is because the relative cost of the ASU increases as the plant size reduces.

Progress since the previous review suggests the TRL for most of the oxyfuel gas-turbine systems is similar to that achieved before. The main exception is NET Power's Allam cycle. Demonstration of process components suggests this technology is at a TRL of 5, with the potential to progress to a TRL of 7 once the 50-MW_{th} demonstration facility is fully operational. As highlighted by the companies, most of the components used in the process are standard. Working with commercial suppliers is reducing the risk associated with the development of the non-standard components, and should assist with future scale-up and deployment.

4.2 Advances in air separation

A commercial-scale coal-fired oxycombustion power plant requires thousands of tonnes of O₂ per day. As a rough guide, a coal-fired oxycombustion boiler requires 19.5 t/d/MW_e, and an NGCC 15.5 t/d/MW_e (Kluiters et al. 2010). Thus, a 500-MW coal-fired power plant requires a constant supply of around 10,000 tonne of O₂ per day (Higginbotham et al. 2011). Currently, the large volumes of moderate purity (~95%) oxygen required can only be met by cryogenic air distillation: a

well-established, commercial process already operating at scales comparable to those required for an oxycombustion plant.

The ASU is one of the largest cost items for an oxycombustion plant, contributing approximately half of the auxiliary power consumption (mostly the air compressor and low-pressure column) and up to 20% of the total plant cost (Lockwood 2016). Emerging technologies aimed at reducing the cost of air-separation processes include membranes (dense ceramic, polymeric) and PSA/VPSA processes. The emerging technologies, however, are at an earlier stage of development, and are not currently able to economically produce large volumes of O₂ at the moderate purity (>95%) required for large-scale oxycombustion.

4.2.1 Cryogenic air separation

Cryogenic air separation is the only commercially available technology that can produce O₂ in the purity and quantities required for oxycombustion processes. The main components of the process include the main air compressor, pre-cooling system, purification unit, heat exchangers, distillation columns and vaporisers/condensers. Air is drawn into the process, compressed (~4 bar) and cooled to remove trace impurities, such as CO₂ and water. The air is then liquefied (–170 °C) and transferred to a distillation column where N₂ is removed as the top product, and O₂ the bottom. Cryogenic air separation is already widely used in industries such as glass, steel and chemical manufacture. These industries often have more stringent requirements for the purity of O₂ produced. The energy required for O₂ production increases steeply for O₂ purity above 95% (Darde et al. 2009). Cryogenic air-separation processes have now been adapted for oxycombustion requirements (lower-purity O₂ (85–98%) at lower pressure (1.3–1.7 bar_a)). Optimisations of this process have already reduced energy requirement from 200 to 140–160 kWh/tO₂ (Darde et al. 2009, Higginbotham et al. 2011). Reductions in energy are often associated with an increase in capital expenditure (Darde et al. 2009). Integration with the host power station is also expected to improve efficiency. The oxyfuel demonstration plant, Callide in Australia and Schwarze Pumpe in Germany, both used cryogenic air-separation systems. Single-train units are currently able to produce 5,000 tO₂/d, with multi-train facilities able to produce much higher quantities. Several techniques used to improve the efficiency of cryogenic air separation are covered in Lockwood (2014):

- 5–7% energy saving estimated through compressor optimisation
- 2–3% efficiency gains through improvements to TSA pre-purification step
- 10% efficiency gain through improvements to cryogenic heat exchange.

Cryogenic ASUs are already highly integrated, which limits the potential for additional energy saving through thermal integration with the oxyfuel power plant. Possibilities include heat of compression recovery and perhaps advanced flue gas heat recovery (Wu et al. 2018).

In the EU-funded O2GEN project, optimisations of the cryogenic air-separation process were investigated. Improvements included adiabatic compression with heat recovery, optimisation of a PSA process for pre-treatment, development of a membrane contactor and design of advanced structured packing. The new ASU configuration reduced net power consumption by 23% in comparison to a reference ASU configuration, resulting in an estimated specific energy of separation of 150 kWh/tO₂ (Espotolero and Romeo 2017).

One possible method for reducing the energy requirement of the air-separation process is to produce lower-purity oxygen. This, however, increases the energy consumption of the downstream CO₂-purification step. This trade-off was investigated by Li et al. (2013), who suggest that targeting an O₂ concentration of 80 mol% results in a minimum combined energy usage of both the ASU and CPU steps. O₂ purity levels below 80 mol% are not recommended as it becomes difficult to achieve 95% CO₂ purity in the downstream CPU.

4.2.2 Air-separation membranes

Despite the efficiency improvements seen for cryogenic air separation, the units still represent the largest energy consumption of an oxyfuel plant. As such, research and development into other air-separation technologies is being explored. A potentially lower-cost method for separating O₂ from air is to use membranes. Research has focused on dense, ceramic membranes made from perovskites or fluorites (Wu et al. 2018). These materials are catalytic and able to break molecular O₂ into O²⁻ ions at high temperatures (800–900 °C). The O²⁻ ions are conducted through the membrane and recombine into O₂ molecules on the permeate side. These types of membranes are known as oxygen separation or ion-transport membranes. To balance the charge, electrons are conducted across the membrane in the opposite direction (or via an external circuit), and hence the membranes should also be electrically conductive (Kluiters et al. 2010). As a result, they are also referred to as mixed-conducting membranes or mixed ionic–electronic conductors. As with most membranes, transport of O²⁻ ions across the membranes is driven by partial-pressure difference of O₂ on either side of the membrane. This can be generated via a pressure difference (compression typically to 5–40 bar), or through combining the membrane into the combustion process, where fuel combustion on the permeate side reduces the O₂ partial pressure. Kluiters et al. (2010) have estimated that for a 1000-MW_e natural-gas-fired power plant, a membrane with a target flux of 10 ml/cm².min would require 80,000 m² of membrane.

Polymeric membranes can separate O₂ from air at ambient temperature. They have the advantage of low price, flexibility and easy handling. However, O₂/N₂ selectivity is usually limited, so oxygen-enriched air, rather than high-purity oxygen, is produced (Chen et al. 2015). Based on current material performances, polymeric membranes are usually considered where medium purity O₂ (30–60%) and small-scale plants (10–25 t/d) are required (Belaissaoui et al. 2014, Haider et al. 2018). Carbon-based membranes separate gas molecules based on molecular sieving, and can have improved separation performance compared with polymeric membranes. Operational stability and ageing, however, are significant development issues (Haider et al. 2018). Where lower-purity oxygen is acceptable, polymeric and carbon-based membranes may see an economic advantage.

While there has been ongoing evaluation of membranes for air separation, the majority of this work is still at laboratory scale (Wu et al. 2018). The two more developed process concepts are the oxygen-transport membrane developed by Praxair, and Air Product's ion-transport membrane. A summary of these technologies, and others that have reached pilot-scale evaluation, is provided in Table 28.

Table 28 Summary of oxygen-separation membranes evaluated at pilot scale

TECHNOLOGY COMPANY/RESEARCH INSTITUTE	DESCRIPTION	COST AND ENERGY INFORMATION	REFERENCES
Ion Transport Membrane Air Products	<p>Square perovskite wafers stacked into modules able to produce ~1 t/d O₂. 5 t/d facility commissioned in 2010. Air is fed at 13 bar and 800–900 °C. Permeate side is vacuum pumped to achieve O₂ partial-pressure gradient across module.</p> <p>100 t/d facility commissioned in 2014. The Intermediate Scale Test Unit integrated O₂ production with gas-fired power generation. O₂ in hot exhaust air leaving membrane module combusted to generate 1 MW net power. The feed air to the membrane is pre-heated by the turbine exhaust, then raised to 800 °C via separate gas-fired heater. 300 h operation with 16 t/d O₂ production have been achieved.</p> <p>Recent focus has been on integration with integrated gasification combine cycle (IGCC) systems and the production of syngas.</p>	<p>For 90% capture, an efficiency gain of 2.5 percentage points and 5% reduction in LCOE over cryogenic ASU is expected (800 MW_{th} supercritical pulverised coal plant).</p> <p>Evaluation completed by EPRI for 765-MW_{th} IGCC plant capturing 87% CO₂. Efficiency increase of 1.8 percentage points, and 10% reduction in LCOE over system using cryogenic air-separation unit (ASU) estimated.</p>	<p>Lockwood 2016 Anderson et al. 2016 DEMOYS 2015</p>
Oxygen-transport membrane (OTM) Praxair	<p>Tubular ceramic membrane on porous support used for O₂ separation. Gaseous fuel supplied to permeate side of membrane with resulting combustion reducing O₂ partial pressure and providing driving force for O₂ transport across the membrane. As separation is driven by O₂ consumption within the tubes, no pressurisation of air feed is required.</p> <p>Several systems considered, with process incorporating two partial-oxidation (POx) reactors upstream of the OTM boiler found to give smallest increase in cost of electricity (COE). Syngas reacted in POx to raise temperature prior to expansion through power recovery turbine. Syngas is then expanded and fed to OTM boiler. OTM provides bulk of O₂ for combustion (~70%) with final O₂ supplied by separate air-separation unit (ASU) (due to decrease in O₂ flux across membrane with lower fuel concentration).</p> <p>Several panels of tubes have been evaluated treating 190 Nm³/h syngas. Ongoing development to focus on integration with IGCC cycles.</p>	<p>Initial economic analysis of combined system with ASU integration and upstream pre-oxidation steps suggests 32.8% increase in COE over DOE reference coal plant, with capture cost ~\$38/tCO₂.</p> <p>For IGCC estimate 10–14% increase in efficiency, 8–12% reduction in COE, 17–39% reduction in carbon-capture cost relative to DOE base case (depending on gasifier type used).</p>	<p>Li 2017 Kelly 2014 Rosen et al. 2011</p>
OXY-COAL-AC RWTH Aachen	<p>As part of the OXYCOAL-AC project a pilot membrane module was constructed. Initial laboratory experiments were conducted on 1 m² tubular BSCF perovskite membranes. A module was then constructed containing 570 membrane tubes (15 m²) capable of operating at temperatures up to 850 °C and pressures up to 20 bar, with the capability of producing 300,000 L O₂ per day (0.6 t/d).</p>		<p>Pfaff et al. 2012</p>
DEMOYS Dense membranes for efficient oxygen and hydrogen separation EU project under FP7 Framework, coordinated by Ricerca Sul Sistema Energetico	<p>Project objective to develop thin mixed-conducting membranes for O₂ and H₂ separation using the low-pressure plasma spraying–thin-film technique.</p> <p>Lanthanum-strontium-cobalt-iron oxide on porous metal support evaluated for O₂ separation on pilot loop operating at 700–950 °C. Issues with cracking resulting from differences in thermal expansion of membrane and support. Modification and sintering of support overcame cracking issues.</p>	<p>Capital cost of OTM-based unit ~35% lower than cryogenic ASU for circulating fluidised-bed (CFB) power plant.</p> <p>LCOE 87.2 €/MWh (12% lower than similar plant using cryogenic ASU). CO₂-avoidance cost 44.8 €/tCO₂ (27% lower than similar plant using ASU).</p>	<p>DEMOYS 2015</p>

TECHNOLOGY COMPANY/RESEARCH INSTITUTE	DESCRIPTION	COST AND ENERGY INFORMATION	REFERENCES
	<p>Based on laboratory evaluation determined O₂ permeability, 114,000 m² membrane estimated required for 650-MW CFB-USC power plant.</p> <p>Future development expected to focus on smaller-scale applications, such as micro gas turbines.</p>	<p>Efficiency of 650-MW CFB–ultra-supercritical power plant with OTM-based oxyfiring estimated to be 40.5% (LHV). 3.8% point lower than reference air-blown plant with no CO₂ capture, 3.8% point higher than plant using cryogenic ASU.</p>	
<p>GREEN-CC Graded membranes for energy-efficient new generation carbon-capture process EU project under FP7 Framework, coordinated by Forschungszentrum Juelich</p>	<p>Aim of project to develop membranes for integrated O₂ generation in cement production, oxyfuel and IGCC power plant.</p> <p>A range of membrane materials evaluated at lab-scale, with LSCF scaled up for evaluation in membrane module (420 cm² membrane area) due to stability in CO₂ and successfully sealed to housing materials using Ag/CuO-based reactive air brazing. Stability to SO_x still an issue. Leakage issues limited long-term evaluation.</p>	<p>Neglecting cost of membrane module, COE for OTM power plant estimated at 98.7 €/MWh. This suggests price of 1,040 €/m² acceptable for membrane module (when compared with COE of reference case).</p> <p>OTM becomes a viable solution when CO₂-emission costs exceeds 96 €/tCO₂</p> <p>Based on costs of developing the test module, an estimate was made for construction costs of the membrane module. Total cost estimated at 16,400 €/m² (LSCF material costs 700 €/m², membrane manufacturing 4,200 €/m², housing and sealing 11,500 €/m²).</p>	GREEN-CC 2018
<p>Lanthanum strontium cobalt ferrite (LSCF) perovskite hollow-fibre membrane Shandong University of Technology</p>	<p>Module containing 889 membranes (9914 cm² of La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-α}) able to achieve 3.1 standard litres per minute (SLM) with oxygen purity of 99.9% at 1070 °C. Production rates increased with temperature, but system failure (particularly seals) noted at temperatures above 1070 °C.</p> <p>1200 h operation achieved at 960 °C producing 99.4% O₂ at 0.84 SLM.</p>		Tan et al. 2010

For both Praxair and Air Products, the current focus is on incorporating their membranes into IGCC facilities and reaction with syngas. Gupta et al. (2016) evaluated a Praxair oxygen-transport membrane for 80 h in an experimental coal gasifier at 850–900 °C. The experimental set-up provided information on material stability in coal syngas, rather than evaluating the efficiency of the overall process. O₂ flux through the membrane was noted to increase with temperature, and also H₂ composition in the syngas (H₂/CO ratio). During the test campaign, no discernible decrease in performance was observed, and the membrane appeared to be stable to syngas and ash components.

An early version of a membrane-integrated process was the Advanced Zero Emission Power Plant, initially proposed by Norsk Hydro. In the initial concept, all oxidation of the fuel took place inside the membrane unit; however, the more recent approach progressed to systems with a separate combustion chamber (Kluiters et al. 2010). They also considered incorporation of the mixed-conducting membrane into a conventional gas turbine. Cost of separation was estimated to be

reduced by 25–35% compared with standard a PCC process using liquid absorbents (Sundkvist et al. 2001). A drawback of the cycle is the temperature limit of the ceramic heat exchangers. This resulted in lower turbine inlet temperatures compared with natural-gas-fired turbines and lower overall efficiency of the process. Other membrane concepts have now been proposed (Kluiters et al. 2010).

Eindhoven University have evaluated mixed ionic–electronic conductor ceramic membranes for the production of small-scale H₂ via an auto-thermal reforming process. These were evaluated at laboratory scale, showing suitable O₂ fluxes across the membrane. Based on the experimental results, an Aspen-based simulation of the process showed reforming efficiencies in the range 62–70% where the auto-thermal reforming membrane reactor is operated at 900 °C (Spallina et al. 2015).

Kerionics, a European-based company, is also offering industrial generation of high-purity O₂ (>>99.5%) using ionic-membrane modules operating at high temperature (1000 °C). They claim a cost reduction between 20–80% compared with current technologies for industrial applications that require oxygen or enriched air. They currently market (portable) generation of oxygen for small scale or in restricted environments (e.g. replacing the use of gas cylinder bundles) by means of modules with a capacity of 2–8 m³/h (100 metric tonnes per annum). The use of multiple membrane modules is suggested for larger-scale applications. They have received Horizon 2020 SME instrument phase 1 funding to assist with development and commercialisation of their technology (Kerionics 2018).

One method for integrating oxygen-separation membranes into an oxyfuel plant would be to use the recycled CO₂ (needed to maintain flame temperature) as a sweep gas for the membrane. This set-up, however, requires the development of components not currently available (e.g. hot clean-up technologies to remove particulate and other components harmful to the membranes). Initial application will likely require feed pressure or permeate vacuum to provide the driving force for O₂ separation across the membrane (Castillo 2011). Other challenges facing ceramic membrane-based oxygen separation include high-temperature, high-pressure sealing, particularly for high-flux materials such as SCF and BSCF. These show substantial creep at high temperatures, making compressive seals impractical (Darde et al. 2009).

Maas et al. (2016) evaluated the cost of a coal-based oxyfuel process using an oxygen-transport membrane (BSCF). A three-year membrane lifetime, a membrane price of 500 €/m² and CO₂ allowances of 40 €/tCO₂ were assumed. 56,000 m² of membrane were required. Comparison was made to an ultra-supercritical, air-fired power plant. A net efficiency of 40.6% (lower heating value, LHV), a LCOE of 82 €/MWh (of which the cost of the membrane contributed 3.7%), and a cost of 31.5 €/tCO₂ avoided were calculated. The specific investment cost was 55% above that of the reference plant. Maas et al. (2016) note, however, that there is significant uncertainty in the costs of ceramic oxygen-transport membranes.

4.2.3 Other air-separation technologies

Today, the most mature technologies for O₂ production are cryogenic distillation and PSA. Cryogenic distillation enables the production of high-purity O₂ (>99%) at a large scale (beyond 100–300 t/d) while PSA produces O₂ concentrations around 95% and is suitable for small-to-medium-scale plant (20–100 t/d).

PSA (and VPSA) processes are already commercially available for air separation. Columns are typically filled with two sorbents. A pre-treatment sorbent removes water and CO₂ from the air, and the main sorbent preferentially adsorbs N₂ over O₂. Zeolites are the most often used adsorbent material (Wu et al. 2018). The co-absorption of O₂ at higher pressures, however, typically restricts PSA (as opposed to VPSA) processes to plants <15 t/d (Kluiters et al. 2010). Air Products' PRISM VSA oxygen generators use molecular sieves and are able to supply up to 300 t/d of oxygen with a purity of 90–93% (Air Products 2014). Oxygen purities >95% are difficult to achieve via PSA processes, because Ar has very similar adsorption equilibrium properties as O₂. Silver-doped zeolites have shown some degree of improved selectivity of O₂ over Ar (Wu et al. 2018). Carbon molecular sieves, which have different adsorption speeds for O₂ and N₂, have also been evaluated for air separation. O₂ diffuses more rapidly into the pores of the adsorbent, and hence the adsorbent is more selective for O₂, producing a stream of enriched N₂. O₂ is then recovered during the regeneration step (Wu et al. 2018). MOFs have been shown to have high O₂ selectivities at low temperatures (77–273 K) due to the higher diffusivity of O₂ compared with N₂ (Wang et al. 2017). Perovskites have also been evaluated for O₂ adsorption (Ikeda et al. 2016, Xu et al. 2018). The ceramic autothermal recovery process (CAR) was developed by the BOC group (currently part of Linde) in the 1990s. The CAR process uses the O₂ storage capacity of perovskite materials, and is essentially a PSA process carried out at high temperature (600–800 °C). A techno-economic assessment of the CAR process for a 1000-MW NGCC plant suggested both power consumption and capital costs were roughly half that of cryogenic ASU (for an ASU producing 99% O₂). The CAR process has been evaluated at 1 t/d scale by the Western Research Institute of Wyoming (Kluiters et al. 2010).

A more novel approach for air separation is chemical-looping air separation (CLAS, Moghtaderi 2010). Like CLC, CLAS makes use of O₂ carriers to separate O₂ from air as part of a looping process (i.e. chemical looping with oxygen uncoupling). However, in the reduction reactor, a sweep gas (steam and/or recycled flue gas) is used to strip O₂ from the circulating O₂ carrier. Where steam is used as the sweep gas, this can be condensed, leaving a high-purity O₂ stream (99%, Zhou et al. 2016). The O₂ stream can then be supplied to an oxycombustion process. Separating the fuel from the looping system makes the process more amenable to solid-fuel combustion compared with CLC. Simulations suggest that the CLAS system power requirement is 75–80% lower than required for conventional cryogenic air separation. Cormos (2018) simulated a CLAS process using copper as the O₂ carrier. They determined a 3% point efficiency improvement for a 500-MW coal-fired power station over a system using cryogenic separation. Gorke et al. (2018) simulated the CLAS process with theoretical O₂ carriers. They showed that if the properties of the O₂ carrier are not optimal, the steam supply from the boiler may not be sufficient to provide the steam/heat required in the CLAS reduction reactor. If this is the case, then additional heat or O₂ would need to be sourced elsewhere. They identified optimal parameters for the O₂ carrier, and screened more than 2,800 potential candidates, identifying 34 promising materials. They found that commonly cited O₂ carriers (Cu, Co and Mn oxides) were not able to achieve auto-thermal reforming, and would require an additional heat input. Zhou et al. (2016) completed a techno-economic assessment of a CLAS process and compared it with a conventional process using cryogenic air separation. For the metal carrier evaluated, CuO-SiO₂, it was determined that to achieve sufficient O₂ production, the reducing reactor needed to be maintained 80–100 °C above the oxidation reactor. This was achieved using external methane firing to heat the reducing reactor. The energy requirement for O₂ production was

75–80% lower than when using cryogenic air separation. The overall project cost of the CLAS plant, however, was higher, and the net present value of the CLAS and cryogenic processes were found to be similar.

Discussion on commercialisation potential and development since previous review

In the previous review it was noted that oxycombustion has already been demonstrated at significant scale (Callide, 30 MW_e) and was given an overall TRL of 7. Cryogenic air separation is already commercial and has a TRL of 9. However, capacities of single-train ASU would need to increase above those currently operating. Air Liquide recently started operation of a 5,000 t/d (5,800 t/d at sea level) oxygen production unit for Sasol in South Africa (Air Liquide 2018). Thus, a full-scale oxycombustion plant would still require multiple ASU trains. Reducing the oxygen purity requirements may assist in reducing the overall cost of oxyfuel combustion processes, with energy demands for the ASU reduced to around 150 kWh/tO₂ suggested. Banaszkiwicz et al. (2014) suggest that further decrease in energy consumption of the ASU is unlikely due to transport and assembly restrictions. This suggests that the scale effect for cryogenic ASU can be considered saturated.

In the previous review, Air Product's ion-transport membrane technology was assessed as being at a TRL of 7, with Praxair's oxygen-transport membrane and the CAR processes at an earlier stage of development (TRL 4). Air Products were set to build a 2,000 t/d demonstration test unit for the ion-transport membrane. However, little information on this unit is available. In Garcia Fayos' (2017) thesis it was suggested that due to company restructuring, Air Product's Ion Transport Membrane is no longer being progressed. While additional research and small pilot-scale evaluation of additional ceramic oxygen-separation membranes has been undertaken, this technology is assessed as being at a similar level of development as that found previously.

Commercial adsorption-based air-separation processes are available; however, absorption capacities limit this technology to scales lower than required for commercial oxyfuel-fired power plant. Most ongoing research and development is still at laboratory scale. Wu et al. (2018) note that the field of adsorption and sorbents is fairly mature, which suggests that the required transformative technology is not likely to be found in the zeolite and carbon-based materials evaluated to date. Chemical-looping air separation is a much newer technology that builds on experience gained through CLC research and development. While CLOU processes have been evaluated at pilot-scale (see chemical-looping section), to date none of these have produced a separated O₂ stream that was then used for a downstream combustion process. As the full process has not yet been evaluated, this technology is assessed as being at a TRL of 3–4.

4.3 Advances in CO₂ purification and flue-gas treatment

Despite being combusted in high-purity oxygen (up to 97%), the CO₂ produced from oxyfuel combustion is typically around 60–75% wet. After CO₂, the main component is water vapour, followed by incondensable components, such as O₂, N₂ and Ar from the ASU and from air leakage, and some impurities (particularly some SO_x and NO_x). Due to the recycle of flue gas, oxyfuel systems can produce higher levels of impurities than standard combustion systems. The downstream requirements of the CO₂ produced will dictate the level of clean-up required in the compression and purification unit. Where CO₂ is to be compressed for transport and storage, it is generally

transported as a supercritical fluid ($P > 100$ bar), which requires any free water phase to be removed (less than ~ 640 ppm) to avoid corrosion. The removal of light gases (Ar, N₂, O₂) is generally also desired to reduce compression and pumping requirements. This is typically achieved in a cryogenic process, where water levels below 10 ppm may be required to avoid ice formation. If the CO₂ is to be used for enhanced oil recovery, then more stringent limits on CO₂ purity may be applied (O₂ < 10 ppm) (Lockwood 2014, Font-Palma et al. 2016).

The bulk of the water vapour is typically removed via cooling and condensation, followed by a TSA process for final removal to low levels. The CO₂ is then fed into the ‘cold-box’ processes, where it is compressed and cooled to cryogenic temperatures to remove the other light gases. This necessitates the removal of water and NO₂ to avoid freezing. Additional SO_x and NO_x is removed to avoid corrosion, and the use of brazed aluminium heat exchangers requires the removal of Hg. The CO₂-rich liquid obtained can be further purified by flash separation (storage) and distillation steps (EOR) (Lockwood 2014). Vent gases from the cold-box processes can still contain appreciable levels of CO₂. If higher capture rates are required, then this CO₂ can be recovered. Capturing CO₂ from vent gases can increase oxyfuel CO₂-capture efficiencies from 90 to 98% (IEAGHG 2006). Different methods can be used for the compression and purification of the CO₂, and several technology vendors offer commercial products. These are summarised in Table 29.

Table 29 Technologies proposed or used by the five main CO₂ purification unit manufacturers (reproduced from Lockwood 2014)

PROCESS	ALSTOM	AIR LIQUIDE	AIR PRODUCTS	LINDE	PRAXAIR
deSO _x	Low-pressure (LP) alkali scrub	LP alkali scrub	Sour compression	LP alkali scrub	Activated-carbon (AC) bed
deNO _x	Selective catalytic reduction	Distillation	Sour compression	LICONOX alkali scrub at pressure	AC bed
Drying	Temperature swing adsorption (TSA) post-compression	TSA pre or post-compression	TSA post-compression	TSA post-compression	TSA post-compression
Hg	AC pre-drying	Adsorption or cryo-separation proposed	None	AC guard bed	AC guard bed
Vent gas capture	None described	Membranes	Membranes	Pressure-swing adsorption (PSA)	Vacuum PSA
Cold box	Ammonia or auto-refrigeration, flash or distillation	Auto-refrigeration, distillation	Auto-refrigeration, distillation	Auto-refrigeration, distillation	Auto-refrigeration, distillation

Air Liquide have evaluated their CPU systems at the CIUDEN (10 tCO₂/d) and Callide (75 tCO₂/d) demonstration projects. At CIUDEN, the low-pressure TSA driers were evaluated, and were used to protect the compressors from acidic condensates. A separate CO₂-refrigerant cycle was used for initial cooling, prior to distillation columns for removal of NO₂ and non-condensable gases. At Callide, the CO₂ flue gas passes through an alkaline scrub, reducing temperature and removing sulfur compounds. The CO₂ is then compressed to 25 bar over four stages using centrifugal compressors. A chilled-water scrub is used to remove NO₂ and cool the compressed gases prior to auto-refrigeration. Typical NO_x behaviour is for 10% to be removed in the low-pressure alkaline scrub, 55% in

condensates after compression, 15% in the dryers and a final 26% in the cryogenic distillation. Mercury is mainly removed in condensates throughout the low-pressure area, reaching less than $0.1 \mu\text{g}/\text{m}^3$ by the cold-box inlet. No corrosion of materials or damage to compressors has been observed. Air Liquide have proposed using a membrane system for additional capture of CO_2 from cold-box vent gases (Lockwood 2014).

Air Products have evaluated their CPU system at the Doosan oxyfuel pilot at Renfrew (6 kW_{th}), on a $0.3\text{-MW}_{\text{th}}$ equivalent slipstream at the Alstom pilot in Windsor, USA and at the Schwarze Pumpe pilot plant, Germany (1 MW_{th}). The demonstration at Schwarze Pumpe evaluated sour compression (SO_x and NO_x removal), autorefrigeration with partial condensation, and membrane-based recovery of CO_2 from the cold-box vent gases (Lockwood 2014, White et al. 2013).

Linde evaluated their CPU process at the Schwarze Pumpe pilot plant ($10 \text{ tCO}_2/\text{h}$). During the evaluation period the CPU system was modified and upgraded, including installation and evaluation of their LICONOX process (alkaline scrub for NO_x removal) (Lockwood 2014). Further evaluation of Linde's CPU processes is being achieved during operation of CanmetENERGY's 1-MW_{th} pilot as part of an ongoing GTI project (Follet 2017).

Praxair completed bench-scale tests and simulation of their CPU technology as part of a wider oxyfuel study with Foster Wheeler for the US DOE. They use a regenerable, activated-carbon-based process for removal of SO_x and NO_x . To achieve near-zero emissions, Praxair have tested vent gas purification using catalytic oxidation for conversion of CO to CO_2 , followed by VPSA for CO_2 capture (Lockwood 2014)

4.3.1 Pre-treatment

The pre-treatment steps for the CPU plant (removal of water and other impurities) are generally well established, as evidenced by the number of commercial vendors offering products. Traditional gas cleaning units (such as FGD for SO_x removal) have been shown to operate with similar performance under oxyfuel conditions (Stanger et al. 2015). As pressure increases, the reaction mechanisms of SO_x and NO_x components in the flue gas are less well established. Hence, there is interest in understanding their removal under higher-pressure conditions. As summarised in the section on pressurised oxyfuel combustion, the majority of ongoing work in that space is around the downstream purification of the CO_2 produced. These projects are summarised in Table 30.

The potential for SO_x and NO_x removal at higher pressures is also of interest during the downstream compression of the CO_2 product. Stanger et al. (2015) evaluated the potential of using the compression circuit for low-cost removal of NO_x , SO_x and Hg from the CO_2 product stream. A bench-scale piston compressor was used to compress a slipstream of the CO_2 flue gas produced at the Callide oxyfuel project over a two-week period. SO_2 was readily captured during compression ($>80\%$ by 10 bar), suggesting that it is a possible passive cleaning option. Residence time impacted NO_x removal, with capture increasing from 55 to 75% when the compression residence time was doubled. This increased to 83% capture with an increase in back-end pressure from 24 to 30 bar. Reducing the compression temperature was noted to increase the capture of NO_x and Hg . Gaseous Hg^0 in the flue gas was effectively removed from the gas stream using the compression circuit. This suggests that a dedicated removal unit, such as an activated-carbon bed, might not be required.

The use of brazed aluminium heat exchangers places a strict limit on allowable mercury in the CO₂ flue gas. Gomez-Gimenez et al. (2017) evaluated a regenerable sorbent based on gold nanoparticles supported on a structured carbon under oxycoal combustion conditions. Under simulated flue-gas conditions, the presence of NO or HCl in the flue gas led to mercury oxidation and retention on the sorbent. The sorbent was also evaluated treating the flue gas from a 3-kW_{th} oxycoal bubbling fluidised-bed combustor. Despite the high SO₂ content, the sorbent achieved a high capture efficiency.

Air Liquide have proposed using current commercial technologies for first-generation oxycoal plants. For sulfur removal, this includes FGD followed by a polishing stage with a sodium reagent. Two strategies are being pursued for second-generation plants: a low-pressure drier to avoid sulfuric acid formation during the compression process, and using NO₂ as reagent for SO₂ conversion to sulfuric acid at low pressure before the flue-gas compressor. For mercury, one management strategy is to have no specific mercury removal unit, as equipment such as scrubbers, flue gas condenser, coolers may remove sufficient mercury, particularly in the presence of strong acids such as H₂SO₄ and HNO₃. A second strategy is adsorption into a guard bed (Tranier et al. 2011).

Table 30 Pre-treatment technologies being evaluated as part of pressurised oxyfuel combustion research

TECHNOLOGY COMPANY/RESEARCH INSTITUTE	DESCRIPTION	COST AND ENERGY INFORMATION	REFERENCES
Transport membrane condenser GTI	Patented transport membrane condenser developed to recover pure water from flue-gas streams. Current DOE sponsored project to adapt and evaluate the technology for pressurised oxycombustion. Pilot-scale, high-pressure modular version of condenser to be built and evaluated as part of project. Commercialised for gas-fired industrial boilers in 2009.	Latent heat recovery expected to boost power-generation efficiency of pressurised oxycoal boiler by up to 14%.	Wang 2017
CO ₂ -purification and heat-recovery system GTI	As part of their ongoing demonstration of pressurised, fluidised-bed combustion system, GTI is also evaluating Linde's direct contact cooler (DCC) (removal of HCl), LICONOX (removal of NO _x and SO _x) and de-OXO (removal of O ₂) systems at CanmetENERGY's 1-MW _{th} pilot plant.		Follett 2016 Follett 2017
Integrated flue-gas-purification and latent heat recovery for pressurised oxycombustion University of Washington at St Louis	Continuing the development of the staged pressurised oxyfuel combustion (SPOC) system, this project will develop bench-scale equipment for the removal of SO _x and NO _x components with simultaneous heat recovery from flue-gas moisture condensation. The simultaneous removal of SO _x and NO _x components is expected to be more economic than the current separate removal steps. Other advantages include restricting the condensation of acid gases to a single vessel, and improved Rankine cycle efficiency with recovery of flue-gas latent heat. A prototype unit is to be developed and evaluated with flue gas from the 100-kW _{th} SPOC combustor.	Early stage techno-economic studies suggest incorporating integrated pollutant removal with SPOC technology increases efficiency of oxycombustion 6% points above first-generation oxycombustion.	Axelbaum 2017
Catalytic removal of O ₂ and pollutants in exhaust gases from pressurised oxy-combustors	Project to develop and validate catalytic materials and systems for purifying flue gas from pressurised oxycombustion.		Lu et al. 2017

TECHNOLOGY COMPANY/RESEARCH INSTITUTE	DESCRIPTION	COST AND ENERGY INFORMATION	REFERENCES
University of Illinois	Reverse-flow, fixed-bed reactor for O ₂ removal via direct reduction of CH ₄ . Multifunctional catalytic packing materials and catalytic DCC design for enhanced oxidation and removal of NO and Hg. Fabrication of small bench-scale units to evaluate with slipstream from SPOC test facility.		

4.3.2 CO₂ purification

CO₂ is typically purified via well-established compression and cooling processes. This can also include the recovery of additional CO₂ from the cold-box vent gases for enhanced capture rates. Current commercial suppliers (Table 24) all use some form of refrigeration and distillation for this step. While other purification techniques have been investigated (e.g. PSA, Chou et al. 2018), the majority of ongoing research has focused on simulating an optimisation of current technologies (Dowling et al. 2014). This includes heat integration between the ASU and CPU, in particular using the cool N₂ stream from the ASU for cooling in the CPU (Zhu et al. 2017), and heat integration with the host power station (Font-Palma et al. 2016).

Besong et al. (2013) evaluated a process for cooling and purifying CO₂ while avoiding the need for a distillation column. The low-temperature, CO₂-purification process is based on a process patented by COSTAIN, and achieves phase separation using simple flash units integrated with the compression process. The cold duty of process streams is used to supply the required refrigeration so that the overall power consumption is low. The processes were simulated in Hysys, and achieved a CO₂ purity of 98% (for storage applications) and >90% capture, provided the dry feed to the CPU unit was >85%.

Discussion on commercialisation potential and development since previous review

Downstream CO₂ purification for standard oxyfuel plants is already fairly well developed. The previous review identified the Linde and Air Liquide pre-treatment technologies as being at a TRL of 7, with Air Products and Praxair at TRL of 6. The cold-box processing technologies have been assessed at a TRL of 8, and extracting residual CO₂ from cold-box vent gases at a TRL of 7. The lack of ongoing oxyfuel demonstration projects has hindered further large-scale development of these technologies, suggesting the TRL is similar to that achieved previously. Ongoing research and development has focused on optimising existing processes, and also taking advantage of the benefits of pressurised oxyfuel combustion. The technologies being progressed by the University of Washington and the University of Newcastle are still at lower stages of development (TRL 4). The processes suggested for the compression and purification of CO₂ employ standard technology, which should assist scale-up of these technologies. Through demonstration projects, particularly those of Schwarze Pumpe and Callide, these technologies have already seen significant demonstration at a decent scale.

5 Pre-combustion capture technologies

Pre-combustion capture involves removing the CO₂ prior to combustion. This can be achieved through gasification of a fuel, or steam reforming of gas, as outlined in Figure 14.

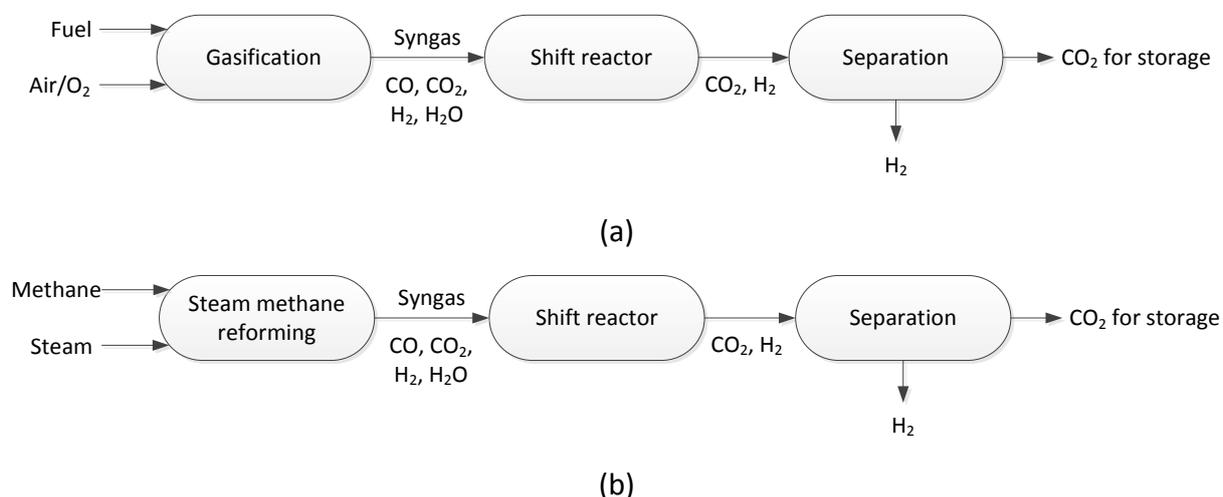


Figure 14 Pre-combustion CO₂ capture process via (a) gasification, (b) steam-methane reforming

CO₂ removal is usually from a syngas mixture comprised primarily of CO₂ and H₂. Pre-combustion capture typically involves the gasification of a carbonaceous fuel (e.g. coal, waste, biomass) or steam methane reforming/partial oxidation of natural gas, generating the syngas. The raw syngas is a mixture of CO, CO₂, H₂, CH₄, N₂, and H₂O, with other trace contaminants depending on the fuel source and technology used. This gas mixture is then cleaned to remove toxic impurities (e.g. H₂S and other sulfur compounds that can poison downstream catalysts) and shifted, via the water–gas shift (WGS) reaction (equation 4), to generate a stream of CO₂ and H₂. The syngas can be combusted (e.g. in gas turbines, boilers or furnaces), or purified H₂ can be produced.



The WGS process generally occurs in two stages: via high-temperature and low-temperature shifts. The gasification process can be either air or O₂-blown. While air-blown systems avoid the need for an expensive upstream ASU, O₂-blown systems are smaller in volume and avoid N₂ dilution of the syngas. CO₂ concentrations can be in the range of 25–40 vol%, at pressures from 20–50 bar (Cowan et al. 2011). At these CO₂ partial pressures, adsorption and physical absorption are typically used for CO₂-capture applications.

Pre-combustion capture technologies are of interest, because power production via IGCC is more efficient than pulverised coal combustion. The syngas is combusted in a gas turbine, generating electricity, followed by a steam turbine for additional electricity generation. Where CO₂ is separated, this can often be achieved at pressures above ambient, reducing compression requirements. In addition, as CO₂ partial pressure in syngas is typically higher than in combustion flue-gas streams, pre-combustion CO₂-capture processes are inherently more efficient than their post-combustion counterparts. An additional benefit of pre-combustion capture is the flexibility in power-plant output, i.e. the ability to switch between H₂ production and power generation. IGCC plants have an

overall heat-to-electric-power efficiency of around 45%. This is higher than most conventional pulverised coal power plants; however, the advantage is offset by higher capital costs. The result is that without CO₂ capture, the electric power produced at an IGCC plant is expected to be 25% more expensive than electricity produced in a sub-critical pulverised coal power plant (Merkel et al. 2012).

In general, research activity into pre-combustion capture has focused on coal more than natural-gas power plants. This is mainly because economic assessments have shown lower costs of CO₂ avoided, and lower plant complexity, for NGCC coupled with post- rather than pre-combustion capture of CO₂ (Jansen et al. 2015). While coal-based gasification systems are widely used industrially for chemical manufacture, IGCC systems have found limited application to date. Operational IGCC facilities (without CO₂ capture) include the Wabash River Repowering Project, Indiana, USA (262 MW, commercial operation since 1999), Tampa Electric IGCC facility (250 MW, commercial operation since 2001), Edwardsport IGCC project, Indiana, USA (618 MW), Nakoso, Japan (250 MW, operational since 2007), and Vresova, Czech Republic (400 MW, operational since 1996).

ELCOGAS operated the Puertollano IGCC plant (Casero et al. 2013). As part of this they operated a 14-MW_{th} pilot plant able to treat 3,600 Nm³/h syngas generated in the power plant (equivalent to 2% of the total syngas produced in the gasifier). The pilot plant captured 100 t/d CO₂ (capture rate >90%) and produced 2 t/d H₂ (99.99% purity). A two-stage WGS process was used, followed by CO₂ absorption using aMDEA. After CO₂ removal, a portion of the H₂-rich stream (77.4% purity) is sent to a final purification step. PSA (activated carbon, alumina and molecular sieve) was used to increase CO₂ purity to 99.99%. Based on the results of their pilot-scale operation, they calculated a cost of CO₂ avoided of 26.35 €/tCO₂ (excluding compression). Nuon Power operated a 253-MW IGCC facility in Buggenum, The Netherlands, from 1994 to 2013. During the end of its operation a pre-combustion capture pilot plant operated onsite, treating a slipstream of the syngas from the facility as part of the CO₂ catch-up project. Sulfur removal was achieved via a Sulfinol desulfurisation unit before being shifted. CO₂ removal was achieved via physical absorption into dimethyl-ether of polyethylene glycol, with regeneration via PSA. 80 to 85% CO₂ was captured, producing a H₂-rich syngas (van Dijk et al. 2014). The project finished in 2013 after >5000 h operation of the pre-combustion capture facility. Since then, progress in pre-combustion capture has stalled, with the abandonment of several planned IGCC demonstration projects. The first proposal of the FutureGen project was for an IGCC process producing electricity and H₂, with CO₂ storage. The project was at the development stage when funding was cancelled in 2008. IGCC technologies were also assessed as part of the Wandoan and ZeroGen projects in Australia. Both projects found that while it was technically feasible to install IGCC with CCS, the capital costs were deemed too high. More recently, Southern Company in the USA started development of an IGCC with CCS plant at their Kemper County facility. In 2017 they switched the facility to burning natural gas in an effort to manage costs.

Despite the challenges faced by demonstration plants, pre-combustion capture technologies have progressed, particularly with a focus on reducing cost. As highlighted in the previous IEAGHG review (2014), the cost of CO₂ capture for IGCC applications is lower than for post and oxycombustion processes. The overall plant costs, however, are higher, and thus technologies addressing cost reductions need to consider the wider plant, including the WGS reactors and gas clean-up technologies. Since the CO₂-capture system accounts for less than 10% of an IGCC plant's total capital requirement, large-scale deployment will require system-wide cost reductions in other major plant components, as well as in overall plant integration, configuration and design (Zhai and Rubin 2018). Analysis of the efficiency losses associated with first-generation pre-combustion

capture technologies applied to IGCC shows that the largest loss is associated with the WGS section (3.5% points). This is mainly due to the steam extraction required for the WGS reaction. Other losses include the CO₂ removal and reduced gas-turbine output (1.7% points), and CO₂ compression and drying (3.0% points) (Jansen et al. 2015).

Coal gasification technology is already well established, finding significant use in the production of chemicals. With the returning interest in H₂ as an energy carrier, it is likely that there will be renewed interest in gasification with CO₂ capture for the production of high-purity H₂. Gasification followed by power-generation (IGCC) technologies, however, are less widely applied today due to complexity and cost constraints. Despite this, IGCC with CO₂ capture is offered commercially. For example, GE offer their standard 630-MW IGCC reference plant with carbon capture, either as initial plant construction or as retrofit, resulting in net CO₂ emissions equivalent to that of an F-class NGCC (Ku et al. 2011). There is also some ongoing development of highly efficient IGCC processes. CRIEPI, Japan, are developing an oxyfuel-fired IGCC system, incorporating CO₂ recycle as with oxyfuel combustion plant. This removes the need to shift the resulting syngas, thereby removing the need for steam extraction from the power system, maintaining a high efficiency after CO₂ capture. Bench and pilot-scale demonstration of the process is currently under way, with commercialisation in 2030 anticipated (Oki et al. 2017).

The following sections discuss four main pre-combustion capture technologies: liquid absorbents, gas-separation membranes, adsorbents and cryogenic separation.

5.1 Absorbents

Absorbents for pre-combustion capture of CO₂ fall into four main categories: physical, chemical, ionic liquid and clathrate absorbents. Each of these is discussed in detail below.

5.1.1 Physical absorption

The high partial pressure of CO₂ in syngas streams makes them amenable to low-energy capture processes, such as physical absorption. Commercially available physical sorbents have already been developed for use in natural-gas upgrading. These include dimethyl ether of polyethylene glycol (Selexol, UOP LLC), methanol (Rectisol, Lurgi), N-methyl-2-pyrrolidone (Purisol, Lurgi), morpholine (Morphysorb, GTI) and propylene carbonate (Fluor) (Theo et al. 2016). For pre-combustion capture applications, Selexol has been widely used in costing studies (NETL 2010). While these technologies are well established, some research has been directed towards identifying additional physical absorbents and improving current processes. Projects that either have achieved, or are scheduled for, pilot-scale demonstration are summarised in Table 31.

To achieve sufficient CO₂ loading, physical absorption processes tend to be operated at low temperatures (room temperature or below). In the case of Rectisol (methanol), operation is at temperatures around -10 °C to avoid solvent loss. In addition, current commercial offerings use hydrophilic absorbents. While this is beneficial in natural-gas upgrading, for IGCC applications the gas stream needs to be cooled to or below room temperature to avoid water condensation in the CO₂ removal plant, decreasing net power and increasing the capital cost of the process. As a result, there has been continued research and development into new physical sorbents that can operate at higher temperatures. Shi et al. (2017) have completed data mining and molecular

simulation to screen physical sorbents for pre-combustion capture applications. Using warm-gas clean-up and avoiding the energy penalty associated with cooling, the syngas can increase the electrical efficiency of an IGCC–CCS power plant by 3 percentage points, and decrease the LCOE by 20% (Siefert et al. 2016).

Table 31 Developments in physical sorbents

TECHNOLOGY COMPANY/RESEARCH INSTITUTE	DESCRIPTION	COST AND ENERGY INFORMATION	REFERENCES
Hydrophobic absorbents National Energy Technology Laboratory (NETL)	To achieve warm-temperature cleaning technologies, NETL are developing hydrophobic absorbents, combining a novel sorbent with Selexol. Novel sorbents evaluated include polyethylene glycol-siloxane sorbent, and an ionic liquid (allyl-pyridinium bis(trifluoromethylsulfonyl) imide). Current project developing absorbents to operate at 25–80 °C, with regeneration at 25–120 °C using low-grade heat available in the IGCC plant. Absorbent is scheduled for pilot-scale evaluation treating a synthetic syngas in 2018.	Process efficiency expected to increase by around 2% points with warm-gas separation, with potential for capital-cost reduction of capture units. Levelised cost of capture of the hybrid polyethylene glycol-siloxane sorbent found to be similar to that of a plant using Selexol. The cost of the ionic liquid-based process was dependent on the cost of the ionic liquid.	Siefert 2017 Siefert 2016

5.1.2 Chemical absorption

Chemical absorbents, which react chemically with the CO₂ in the syngas, have also been considered for pre-combustion applications. They tend to have higher energy requirements than physical sorbents due to the thermal energy required for regeneration. A commonly used liquid absorbent is BASF’s activated MDEA (aMDEA), as used at the ELCOGAS CO₂ capture pilot plant. Both the CO2CRC and SRI International have developed additional chemical absorption liquids for pre-combustion capture applications. Their technologies are summarised in Table 32.

Asif et al. (2015) have considered a blend of AMP and NH₃ for removing CO₂ both before and after the turbine in an IGCC plant (Aspen simulation). The IGCC with CO₂ removal post-combustion was more efficient. Other absorbents considered include MEA and chilled ammonia, though experimental evaluation of these technologies is lacking. Bonalumi and Giuffrida (2017) have used Aspen simulation to evaluate both MEA and NH₃ processes for PCC from an air-blown IGCC.

Table 32 Chemical absorption research for pre-combustion capture of CO₂

TECHNOLOGY COMPANY/RESEARCH INSTITUTE	DESCRIPTION	COST AND ENERGY INFORMATION	REFERENCES
K ₂ CO ₃ CO2CRC University of Melbourne	CO2CRC has a patented process for high-temperature (>120 °C) pre-combustion capture using K ₂ CO ₃ (UNO MK1). Operating at high temperature reduces syngas pre-cooling requirements and increases syngas water content, both of which improve IGCC power plant output.	CO ₂ -capture efficiencies of 56% achieved, with regeneration-energy requirement ~4.5–4.9 GJ/tCO ₂ estimated after accounting for heat losses.	Smith et al. 2012 Urech et al. 2014 Li et al. 2015 Anderson et al. 2011

	Evaluated both un-promoted 30 wt% K ₂ CO ₃ , and 30 wt% K ₂ CO ₃ -promoted with 3 wt% boric acid at pilot scale (30–50 kg/h CO ₂) treating a syngas slipstream from the HRL Laboratories' research gasifier (air-blown, fluidised bed). The pilot operating temperature was lower than the patented process, and unshifted syngas was supplied from the gasifier. The promoter was found to provide no benefit. Co-absorption of hydrocarbons from the syngas was thought to lower surface tension, leading to foaming issues towards the end of the trial. Low ambient temperatures also caused some unwanted bicarbonate precipitation during start-up.	Pilot-scale results used to validate Aspen simulation. Simulation suggests 1% point increase in overall efficiency of IGCC with 90% CO ₂ capture via hot K ₂ CO ₃ compared with Selexol-based process. Smaller absorber also required for K ₂ CO ₃ case. Heat integration between CO ₂ compressors and sorbent regeneration observed to raise overall efficiency by further 0.3–0.7 % points.	
Ammonium carbonate–ammonium bicarbonate (AC-ABC) process Aqueous solution of ammonium carbonate SRI International	Simultaneous removal of CO ₂ and H ₂ S from syngas at 40–60 °C. Regeneration completed at high pressure (20–50 bar), reducing CO ₂ compression requirements. Bechtel's pressure-swing Claus sulfur-recovery unit used to convert captured H ₂ S to elemental S. Bench-scale and small pilot-scale (0.15 MW _e) evaluation achieved, treating shifted syngas at the NCCC (700 h). CO ₂ and H ₂ S capture greater than 99% demonstrated.	Cost of electricity (COE) increase estimated at 30% (c.f. 41% for Selexol), with cost of CO ₂ capture \$27/tCO ₂ . First year COE 133.7 \$/MWh (c.f. 102.6 \$/MWh for IGCC with no capture, 144.8 \$/MWh for Selexol-based process).	Nagar et al. 2016

5.1.3 Ionic liquids

While ionic liquids have been considered for pre-combustion applications, they suffer from similar problems as identified under PCC, namely high cost and high viscosity. Siefert et al. (2016) evaluated the ionic liquid allyl-pyridinium bis(trifluoromethylsulfonyl) imide for pre-combustion capture. When compared with Selexol, the ionic liquid has similar CO₂ solubility, similar H₂S solubility, lower vapour pressure, higher mass density and lower water uptake. The viscosity is also reported to be lower than other ionic liquids considered, but four times higher than Selexol at 25 °C. An Aspen simulation was used to provide a techno-economic assessment of the ionic-liquid-based process, with capture cost determined to be highly dependent on the cost of the ionic liquid.

Basha et al. (2014) evaluated two ionic liquids (TEGO IL K5, TEGO IL P51P) as physical absorbents for the capture of CO₂ from a shifted syngas stream. The ionic liquid's physical properties and gaseous solubilities were evaluated at laboratory scale, and used to build an Aspen simulation. The simulation showed the ability of the two ionic liquids to capture 90% of the CO₂.

Zhai and Rubin (2017, 2018) completed a techno-economic assessment of the ionic liquid 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide as a physical solvent for pre-combustion capture, following a similar process as proposed by Basha et al. (2014). The energy penalty of the process was determined to be predominantly from process and product compression and solvent pumping, with compressors and absorbers being the main capital cost items. The minimum cost of CO₂ separation was found to occur at 90% CO₂ capture. The cost of CO₂ avoided was estimated at \$62/tCO₂. Implementation of ionic-liquid-based CCS was noted to decrease net plant efficiency by more than 9 percentage points, and increase plant LCOE by \$35/MWh. Comparison to a Selexol-based process showed similar cost of CO₂ avoided, suggesting the ionic-liquid-based CCS system could be a viable alternative process. They note, however, that the simulation completed here did not take into account the effect of impurities, such as water vapour and CO. Also, mass transfer and pressure drop rate correlations derived empirically for conventional solvents with lower viscosity

than the ionic liquid were used in the simulation. Thus, there is a need for additional data, particularly experimental data treating real syngas streams, to fully evaluate this process.

As with PCC applications, most of the ionic liquid development for pre-combustion capture has been at laboratory scale, with no notable pilot-scale demonstrations completed to date.

5.1.4 Clathrates

Clathrate hydrates are crystalline compounds consisting of host water molecules that are hydrogen bonded to form cages encapsulating different guest molecules (Horii 2018). These first came to prominence in natural-gas processing, where methane hydrates were observed to block pipework. Hydrates form in aqueous solutions under high-pressure and low-temperature conditions, and can be used to separate CO₂ from a gas mixture. While they have been assessed for PCC, they are better suited to the higher pressures of pre-combustion CO₂ capture.

CO₂ separation via hydrate formation avoids the need for heat input for absorbent regeneration. The hydrates have high storage capacities, are environmentally benign and can achieve simultaneous capture of H₂S, reducing pre-treatment requirements. They can also produce CO₂ at elevated pressures, reducing product compression costs. Absorber towers are not required, potentially reducing capital costs; however, cooling/refrigeration process are needed. At 275.6 K, the minimum pressure required to form pure CO₂ and pure H₂ hydrates are 1.6 and 366 MPa, respectively. This significant difference in hydrate formation conditions forms the basis of hydrate-based gas separation. To form CO₂ hydrates in a suitable time scale, higher pressures are required, potentially requiring compression of the IGCC syngas (typically 2–7 MPa), adding a potential cost to the process (Babu et al. 2015).

One method for reducing the formation pressure is to add promoters that reduce the equilibrium hydrate formation pressure. Tetrahydrofuran, cyclopentane, propane and H₂S have been evaluated as potential promoters. Another method to achieve hydrate formation under milder conditions is to promote the formation of semiclathrates. In semiclathrate hydrates, both guest and water molecules form the host framework, and also occupy the cages in the structure. Tert-n-butylammonium bromide (TBAB) and tetra-n-butyl ammonium fluoride (TBAF) addition has been evaluated for semiclathrate formation with H₂/CO₂ mixtures. Hydrate-based capture is generally limited to capture rates of less than 70% in a single stage, with potential to increase to 90% capture in two stages. Product purity in principle can be high, but decreases as the concentration of promoter additives is increased (Lockwood 2016).

Research into the use of clathrates for CO₂ capture is being progressed by Keio University (Horii and Ohmura, 2018), Heriot-Watt University (Gholinezhad et al. 2011), Pusan National University, the Korea Institute of Industrial Technology (Kim et al. 2011), University of British Columbia (Linga et al. 2007), the National Institute of Science and Technology, Korea (Park et al. 2013), and the National University of Singapore and Shanghai Jiao Tong University (Zheng et al. 2017).

One of the more developed processes using hydrates for CO₂ capture is the Simteche process, developed by the Los Alamos National Laboratories. Information on this technology is summarised in Table 33.

Table 33 Pre-combustion capture of CO₂ using clathrates

TECHNOLOGY COMPANY/RESEARCH INSTITUTE	DESCRIPTION	COST AND ENERGY INFORMATION	REFERENCES
Simteche Los Alamos National laboratories Nexant Simteche	Cooled shifted syngas fed to reactor at 70 bar and 1 °C where CO ₂ and H ₂ S in the syngas form hydrates. Completed phase equilibrium evaluation of clathrate formation for CO ₂ /H ₂ /H ₂ S mixtures. Addition of H ₂ S increased clathrate equilibrium temperature compared with pure CO ₂ . Bench-scale continuous-flow apparatus used to evaluate time dependence of hydrate formation. Operated at 6.9 MPa and temperatures just above 0 °C. Hydrate formation observed with residence times of only a few seconds in the reactor tube. Pilot-scale evaluation was planned; however, it is unclear if this was achieved.	Single-stage process achieved 64% CO ₂ removal. Preliminary economic analysis estimated CO ₂ -capture cost of \$9/short ton CO ₂ (c.f. \$19 for Selexol, also 64% capture). Simteche process also estimated to have \$40m lower capital-cost requirement c.f. Selexol. For 90% CO ₂ capture, 2-stage process was used. 2-stage process only able to achieve 7% reduction in CO ₂ -avoided cost compared with Selexol process at a similar COE. Babu et al. (2015) provide the COE as 61.3 \$/MWh for a 2-stage Simteche process, compared with 62.4 \$/MWh for Selexol based process.	Deppe et al. 2004 Nexant 2006 Yang et al. 2011 Babu et al. 2015

Several significant technical challenges still remain for pre-combustion CO₂ removal via hydrate formation. Stirred-tank reactors are widely used to study the kinetics of hydrate formation at laboratory scale. However, heat-transfer limitations suggest this type of reactor will be unfavourable for significant scale-up (Mori 2015). In addition, residence times of up to hours can be required for bulk quantities of hydrates to form. Thus, short induction times must be demonstrated if industrially applicable hydrate formation rates are to be achieved. Where free-flowing continuous reactors are used, the potential for gas hydrates to plug pipelines is still an issue. Key engineering process design parameters, such as kinetic rate constants and heat-transfer rates, are not accurately known for CO₂ hydrate formation in continuous-flow systems, since the process fluid becomes a three-phase mixture (Yang et al. 2011). New approaches include using fixed-bed reactors with porous medium, unstirred reactors with immiscible promoters, slurry bubble columns and fluidised-bed columns (Babu et al. 2015).

Discussion on commercialisation potential and development since previous review

CO₂ removal via absorbents, ionic liquids or clathrates was not covered in the previous review. The development of new physical absorbents is at laboratory scale, and hence at a TRL of 3–4. This is expected to increase to a TRL of 5–6 after the planned pilot-scale evaluation by NETL. New chemical absorbents (UNO MK1, AC-ABC process) have achieved small pilot-scale evaluation, and thus their technology readiness is assessed as being at a TRL of 5. While CO₂ removal via clathrate formation has also been investigated for CO₂ removal from natural gas, work is still very much at the laboratory scale evaluating synthetic gas mixtures; hence, the TRL is assessed at 2–3. The most developed process using clathrates appears to be the Simteche process evaluated by Los Alamos National Laboratories and Nexant; however, it is unclear whether the planned pilot-scale evaluation of the process was undertaken. As such, the TRL is assessed as being at level 3–4.

The scale-up of physical and chemical absorbents would be fairly straightforward, as the processes use the same technologies as current liquid-absorbent processes. CO₂ removal via clathrate formation would be challenging, and solutions still need to be found for dealing with the formation of solids and suitable heat transfer in the reactors. If novel reactors are required, this will limit the scale-up potential.

5.2 Gas-separation membranes

Advances in membrane development applied to pre-combustion CO₂ capture can include O₂, H₂ and CO₂-separation membranes. As with oxyfuel combustion systems, O₂-blown gasifiers require an upstream ASU. As such, O₂ separation membranes have the potential for reducing the cost and size of this process step. The technology developments in this area are the same as those outlined for oxyfuel systems, and so are not repeated here. H₂ and CO₂ separation membranes are applied downstream of the gasification and syngas clean-up steps. The higher partial pressure of CO₂ in syngas mixtures suggests membranes could be more suited to pre-combustion removal of CO₂. However, to be competitive with current commercial chemical and physical sorbents, membranes should be applicable to the separation of warm syngas, or even integrated into the WGS process. The high-temperature conditions, particularly in the presence of steam and impurities, are a demanding environment for most existing membrane materials (Lockwood 2016).

In the case of natural gas-based pre-combustion removal of CO₂, membranes can be incorporated into the steam reforming or WGS steps. From a techno-economic perspective, however, it is favourable to integrate the membrane with the WGS process (Peters et al. 2017).

5.2.1 H₂-separation membranes

A wide variety of membrane materials have been considered for the separation of H₂ from syngas, including inorganic H₂ permeable membranes (Pd, Pd alloys), ceramics, carbons and zeolites. The purity of separation required depends on the end use of the H₂ and CO₂, and can affect the choice of membrane used for separation. For IGCC applications, final H₂ purity requirements are not as stringent as for the production of industrial grade H₂ (Ku et al. 2011). This is because H₂ requires dilution before it can be combusted in existing gas turbines. Where the gasification process is oxygen blown, this can be achieved using N₂ from the ASU as a sweep gas on the permeate side of the membrane. While there has been limited uptake of IGCC technologies in recent years, coal gasification (and CO₂ removal) for H₂ and chemicals manufacture is more prominent. With the growing interest in H₂ economy applications, recent work in the pre-combustion capture of CO₂ has tended to focus on H₂ production applications. For applications such as fuel cells, very high-purity H₂ is required (>99.99%). The separation and purification of the H₂ can account for half of the production costs (Castro-Dominguez et al. 2017). Where CO₂ is being captured for storage or EOR applications, CO₂-purity specifications impose a H₂/N₂ selectivity requirement.

Dense, metallic, Pd-based membranes have been widely investigated for the separation of H₂, due to their theoretical infinite selectivity towards H₂ and their high stability in steam at the high operating temperatures experienced under WGS conditions (Guazzone et al. 2012). Pd dissociates H₂ into H⁺ ions, which are then able to diffuse through the membrane before recombining on the permeate side. This separation method means that very high-purity H₂ permeate streams can be

achieved. The high cost of metal membranes, particularly Pd-based membranes, has limited their application to date. Other challenges include stability, such as H₂ embrittlement and sensitivity to sulfur compounds (Merkel et al. 2012). Metal membranes can undergo phase changes at low temperature (<300 °C), leading to catastrophic failure due to H₂ embrittlement. S fouling can lead to lattice expansion and inhibition of H₂ dissociation and recombination. Pd in particular is susceptible to S compounds, CO₂, NH₃ and chlorine, all of which are present in syngas streams (Scholes et al. 2010). To be cost competitive, the lifespan of metal membranes also needs to be increased.

In an effort to produce lower-cost, H₂-separation membranes, Dolan et al. (2018) have considered V-Pd composite membranes. They note that V-based membranes can also suffer from embrittlement. However, this can be minimised through choice of suitable membrane geometry and operating procedures. Ensuring the membrane is only exposed to H₂ at the desired operating point avoids hydride phase transitions and miscibility gaps, minimising the impact of embrittlement. However, these membranes are not suitable for incorporation with WGS catalyst-packed beds in catalytic-membrane reactor modules (Dolan et al. 2015).

Porous ceramic and zeolite-based membranes have also received attention for H₂ separation. Sulfur tolerance is less of a problem for ceramic materials, but the effect of steam on long-term stability is a concern (Ku et al. 2011). These materials have carefully controlled pore structures and generally separate on the basis of molecular size; the smaller hydrogen molecule passes through, while larger species are retained. Alternatively, if the pore sizes are larger, Knudsen diffusion can occur. In this case, separation is based on the difference in the mean path of gas molecules due to collisions with pore walls (Scholes et al. 2010). Despite decades of research, inorganic membranes are still difficult to make into robust, large-scale modules, which has limited their application (Merkel et al. 2012).

High-temperature polymers have also been considered for H₂/CO₂ separation from syngas. Non-porous polymeric membranes operate by the solution–diffusion mechanism, where the permeating gas dissolves into the polymer at one face of the membrane, diffuses across the membrane and is then desorbed at the downstream face. Permeability is thus a function of both gas diffusivity and solubility (Scholes et al. 2010). Compared with inorganic membrane materials, polymeric membranes exhibit lower hydrogen permeances and lower H₂/CO₂ selectivities (Merkel et al. 2012). The lower permeance of polymer membranes can potentially be offset by their lower cost, stability to sulfur compounds and ease of fabrication. However, advanced module designs with innovative staging may be necessary to achieve selectivity requirements (Ku et al. 2011). For IGCC applications, where purity requirements are less stringent, the lower selectivity of polymeric membranes is less of an issue. Polymeric membrane choice depends on the stability of the membrane in the process environment. In particular, exposure to condensing gases, such as CO₂, water and H₂S, can cause plasticisation and subsequent mechanical failure (Scholes et al. 2010).

The Korea Institute of Energy Research evaluated a laboratory pilot-scale, Pd-Cu membrane–WGS process treating a synthetic syngas (1 Nm³/h). The system evaluated a commercial WGS catalyst, with downstream H₂ separation via five membranes in series. The pressure in the system allowed for H₂ production across the membrane, and increased CO₂ concentration in the retentate from 5–80 vol% (Lee et al. 2012). CIEMAT (Sanchez et al. 2014) evaluated a bench-scale Pd membrane reactor for H₂ separation from syngas. While the production of a high-purity H₂ permeate stream was possible, the presence of other syngas components (N₂, H₂O, CO₂) was noted to lower H₂

permeation. When CO₂ was present, the reverse WGS reaction was also observed. H₂-separation membranes were also assessed for IGCC applications under the EU FP7 project M4CO₂ (energy-efficient, MOF-based, mixed-matrix membranes for CO₂ capture). Mixed-matrix membranes based on polybenzimidazole and ZIF-8 nanoparticles were assessed. The addition of the ZIF-8 particles clearly increased membrane performance (Sanchez-Lainez et al. 2016). This project progressed the membrane technologies from TRL 1 through to TRL 4, though larger bench-scale evaluation proved problematic. This technology will be further developed in a follow up H2020–NMBP project (MEMBER) targeting a TRL of 7 (M4CO₂ 2018).

While several H₂ selective membranes have been evaluated at laboratory scale, only a few have made it through to pilot-scale evaluation, particularly treating real gasifier syngas. Table 34 summarises some of the research that has progressed from laboratory-scale evaluation.

Table 34 H₂-separation membranes for pre-combustion capture of CO₂

TECHNOLOGY COMPANY/RESEARCH INSTITUTE	DESCRIPTION	COST AND ENERGY INFORMATION	REFERENCES
MFI-type zeolite membrane reactor Arizona State University	Following successful laboratory-scale evaluation, Arizona State University are continuing a DOE-funded project evaluating the scale-up of the combined water–gas shift (WGS) and H ₂ separation process. The membrane module, containing 21 membrane tubes, is to be evaluated on a raw synthesis gas from a coal gasifier at the University of Kentucky. The system is anticipated to produce 2 kgH ₂ /day. Single-tube membranes have been evaluated for more than 6 months under WGS conditions at 500 °C and 26.5 bar. One week’s evaluation was also completed with syngas containing 1000 ppm H ₂ S, showing stability to a high S environment.		Wang et al. 2014 Dong et al. 2015 Meng and Lin 2018
Hollow-fibre membrane reactor SRI International	The process uses a temperature-stable polybenzimidazole (PBI) polymer membrane to separate syngas at 200–250 °C. The PBI membranes are thermally stable up to ~300 °C and are S tolerant. 50-kW _{th} membrane module evaluated for 600 h at National Carbon Capture Center (NCCC) in 2017. Gen-1 membranes evaluated for 500 h, Gen-2 for 48 h. Were able to achieve greater than 90% recovery at operating temperatures >190 °C. Collaborating with Generon (specialises in manufacture of hollow-fibre membranes) in membrane fabrication scale-up and module fabrication. Future work to evaluate Gen-2 membranes on syngas from O ₂ -blown gasifier.	Cost estimate with Gen-1 membranes suggests CO ₂ -capture cost of ~\$40/tCO ₂ , compared with \$52/tCO ₂ for IGCC with baseline technology (Selexol). Gen-2 membrane achieves H ₂ /CO ₂ selectivity ~40 and 100 GPU (recovers 99% H ₂ with 88% CO ₂ capture). Economic assessment using Gen-2 membrane and Selexol for S removal achieved increase in COE of 18.5% (compared with IGCC with no capture, NETL target 20%).	Jayaweera 2017
Carbon molecular sieve membranes Media and Process Technologies University of Southern California	86-tube ceramic membrane reactor (0.76 m ²) evaluated on a syngas slipstream from gasifier at the NCCC for >300 h. The membrane reactor combines pre-treatment, water–gas shift and H ₂ separation processes. The membrane reactor successfully rejected tar-like species present in the syngas without any evidence of fouling as long as the operating temperature was maintained above 250 °C. Membrane permeation properties also remained unchanged throughout the evaluation period.	Techno-economic assessment of dual-stage membrane process showed 3% higher power output, 3.4% lower capital cost and 7.1% lower cost of CO ₂ capture compared with NETL base case IGCC process (case B5B).	Parsley et al. 2014 Tsotsis et al. 2018 Media and Process Technology 2017

TECHNOLOGY COMPANY/RESEARCH INSTITUTE	DESCRIPTION	COST AND ENERGY INFORMATION	REFERENCES
	Follow-on project used Pd-Ag alloy membrane for residual H ₂ recovery from the CO ₂ product stream. Achieved 150 h evaluation at NCCC.		
Doped polybenzimidazole membranes University at Buffalo	Evaluated doped polybenzimidazole membranes for H ₂ separation from syngas mixtures. Membranes doped with H ₃ PO ₄ were found to have a high H ₂ /CO ₂ selectivity of 140 at 150 °C. Collaboration with MTR and Helios-NRG to develop a mixed-matrix membrane for H ₂ separation. The approach links cross-linked polymers with strong size-sieving ability and Pd-based nanomaterials with high H ₂ /CO ₂ selectivity. The aim is to achieve a membrane with a H ₂ /CO ₂ selectivity of 30, permeance of 500 GPU, and able to operate at 150–200 °C. Membranes have been evaluated in synthetic syngas, and demonstrated stability in the presence of H ₂ S.		Zhu et al. 2018
Pd H ₂ separation membrane SINTEF Reinersten AS	SINTEF has patented a technology to produce Pd-alloy membranes with thickness down to 1–2 μm. Thinner membranes increase H ₂ flux, reducing cost, but also face challenges with potential defects and leakage. A 2-step manufacturing process using a sacrificial glass support and magnetron sputtering is used to produce the membrane film. This film is then wrapped around a porous stainless-steel support, allowing manufacture of membranes of various sizes. SINTEF recently scaled up their membrane manufacturing process, preparing a 19-tube H ₂ separation module with an active membrane area of 2.7 m ² . This module is designed to operate at 450 °C and 50 bar _g . A membrane skid capable of handling 2.7 t/d (200 Nm ³ /h) syngas has now been constructed, with evaluation of the skid at the Statoil 2500 MTPD methanol synthesis plant in Tjeldbergodden scheduled for 2017.		Peters et al. 2017
Polybenzimidazole (PBI) membrane Los Alamos National Laboratories	Laboratory-scale evaluation identified PBI as a promising membrane for pre-combustion capture due to its high sulfur tolerance, high-temperature stability (<450 °C), good mechanical properties and material processing ability. PBI membranes found to exhibit H ₂ /CO ₂ selectivities and H ₂ permeabilities greater than commercial polymeric membranes. First-generation membranes coated on metallic substrate; however, this resulted in high capture costs and large membrane footprint. To increase packing density and reduce costs, hollow-fibre membranes were evaluated. When evaluated in a wet synthesis gas stream H ₂ permeance of 120 GPU and H ₂ /CO ₂ selectivity of 20 achieved at 250 °C over several days operation for the hollow-fibre membranes.	Preliminary techno-economic assessment based on Aspen simulation suggests cost of electricity (COE) 94 \$/MWh (c.f. 105 \$/MWh for Selexol-based process), 21% increase over no capture case (c.f. 34% increase for Selexol).	O'Brien et al. 2009 Singh and Berchtold 2016

TECHNOLOGY COMPANY/RESEARCH INSTITUTE	DESCRIPTION	COST AND ENERGY INFORMATION	REFERENCES
Proteus Membrane Technology and Research	Rigid glassy polymeric membrane that selectively permeates H ₂ . H ₂ /CO ₂ selectivity ~15 at 150 °C.	Techno-economic analysis assumed membrane skid cost of \$500/m ² . Membrane process combined with cryogenic process for final CO ₂ purification. Total plant cost for H ₂ membrane process (with co-separation of H ₂ S) was about 50% the cost of process using Selexol. 20% increase in levelised COE over IGCC with no capture (c.f. 30% increase for Selexol based process).	Merkel et al. 2012
Dense metal membrane Eltron Research and Development	Composite metal membrane expected to be 10x cheaper than comparable membranes made primarily from Pd. The composite membrane consists of a dense metal alloy core, with thin catalyst layers (for H dissociation and recombination) deposited on either side. These membranes are capable of operating at 250–450 °C, and differential pressures up to 70 bar. The DOE-funded test program included pilot-scale evaluation of the membranes at Eastman Chemical's gasifier in Kingsport; however, little information is available on the results of this evaluation.	A preliminary techno-economic assessment suggests a reduction in the COE from IGCC with Selexol from 115.5 \$/MWh to 100.4 \$/MWh for the membrane-based process.	Mundschau et al. 2006 Eltron 2011
Pd and Pd- alloy membranes Worcester Polytechnic Institute	A range of composite membranes have been evaluated at NCCC, including Pd, Pd-Au, Pd-Pt, and Pd-Au-Pt membranes. The membranes were prepared on porous stainless-steel supports, and exposed to sulfur-free, H ₂ -enriched syngas. The membranes (7–14 μm thick, 200 cm ² permeable area) showed an initial rapid decline in permeance on exposure to the syngas, thought to be due to possible surface and/or bulk poisoning. After an initial decrease, performance stabilised with long-term (200 h) stability at 450 °C and 12.6 bar. Where leakage did not occur, high H ₂ purities were obtained (>99%). Pure Pd membranes were noted to fail after ~200 h of operation on the H ₂ -enriched syngas. The harsh environment was thought to reduce their stability, leading to the formation of pinholes in the membrane. The Pd-Au membranes were shown to display the most stable permeance and purity characteristics. They suggested that the Au may act as a patch paste, blocking defects in the Pd layer, improving longevity.		Guazzone et al. 2012 Mardilovich et al. 2015 Castro-Dominguez et al. 2017

Franz et al. 2014 completed an economic comparison of an IGCC process with CO₂ capture using Selexol or a H₂-selective porous ceramic (molecular sieve) membrane. A membrane cost of 300 €/m² and a three-year lifetime were assumed. The membrane process reduced the overall efficiency from 47.4% (LHV, no capture) to 38.3% (37.1% for Selexol). A membrane area of 51,800 m² was required. The COE increased from 45.3 €/MWh for the reference IGCC process to 56.5 €/MWh (57.7 €/MWh for Selexol).

Membranes have also been evaluated for inclusion into the reforming of natural gas. As the steam-reforming reaction and hydrogen-separation processes proceed in a single reactor, a membrane reformer is more compact and efficient than a conventional steam methane reformer with a PSA system. Tokyo Gas has demonstrated a high-efficiency, Pd-membrane natural-gas reformer (40 Nm³/h H₂, 150 kW_{th}), with a hydrogen production efficiency of 81.4%. CO₂ in the off-gas is 70–90%, allowing for easy liquefaction. This is estimated to be 10–15% more efficient than a conventional steam methane reforming/PSA system (Kurokawa et al. 2011).

5.2.2 CO₂-separation membranes

The primary advantage of using CO₂ selective membranes is that the H₂ product can be retained at high pressure, which improves the efficiency of the gas turbine in an IGCC process (Lockwood 2016). Developing membranes that retain the smaller H₂ molecule, but permeate the larger CO₂ molecule is challenging (Scholes et al. 2010). For porous inorganic membranes, this can be achieved by surface diffusion of capillary condensation, generally through the addition of a polymer with CO₂ affinity chemisorbed onto the walls of the pores. However, for surface diffusion to be effective, the pore diameter must be less than 3–4 times the diameter of CO₂, otherwise diffusion of H₂ through the void space in the membrane would eliminate any selectivity (Scholes et al. 2010). Polymeric membranes can be CO₂ selective if they favour solubility selectivity over diffusivity selectivity (Scholes et al. 2012), as CO₂ is more condensable than H₂. Rubbery polymeric membranes typically have these capabilities.

Ohio State University is developing facilitated transport membranes to separate CO₂ from syngas. The amine-containing, CO₂-selective layer enhances CO₂ transfer through the membrane via reaction with amino groups, while hydrogen is rejected due to the absence of reaction (Ho 2018).

The Research Institute of Innovation Technology for the Earth (Japan) have developed molecular-gate membranes for CO₂ separation from IGCC syngas (dendrimer/polymer hybrid membrane). In the membrane, CO₂ reacts with amino groups to form either carbamate or bicarbonate, which acts as a gate to block the passage of H₂, leading to high CO₂/H₂ selectivities. These have been evaluated at laboratory scale at pressures up to 2.4 MPa (Kai et al. 2017).

CO₂CRC and the University of Melbourne evaluated three rubbery polymeric membranes: poly dimethyl siloxane (PDMS), cross-linked polyethylene glycol and poly(ether-b-amide) (PEBAX 2533). These were evaluated at treating an unshifted syngas from a pilot-scale air-blown gasifier. The performance of all three membranes was noted to decrease when exposed to the gasifier syngas, with CO₂ permeabilities decreased compared with laboratory results. This was thought to be due to competitive sorption of other gas components. For the hydrophobic PDMS membrane, the permeability of other gas species also declined, so that selectivities remained relatively unchanged. Further decrease in the performance of the PDMS membrane was observed with long-term exposure over 24 h due to fouling of the membrane (Scholes et al. 2012).

MTR have evaluated their Polaris CO₂ selective membrane under IGCC conditions. These were evaluated at the NCCC treating a gasification syngas. Initial membrane tests were on semi-commercial, spiral-wound modules (1–4 m²), followed by a demonstration system (10–40 m²) treating 227 kg/h syngas (0.15 MW_e equivalent). The enriched CO₂ stream is treated to remove H₂S and H₂O, and cooled to produce liquid CO₂. The syngas feed to the membrane module contained

~9% CO₂. This was increased to ~95% CO₂ in the produced liquid, capturing 60–70% of the feed CO₂. The demonstration skid operated for 400 h, with no degradation of membrane performance observed (Lin et al. 2014). Following this evaluation, a techno-economic assessment was completed for the membrane/cooling system treating the syngas from a 556-MW_e GE gasifier-based IGCC system. The cost of CO₂ capture was noted to increase substantially above 80% capture. At 90% capture, the energy requirement of the membrane system was comparable to the reference plant using Selexol. Total plant cost, however, was lower, at \$192 million compared with \$252 million for the Selexol process. CO₂ production cost was \$17/tCO₂, compared with \$30/tCO₂ for the Selexol process. Capture cost was found to depend on both CO₂ partial pressure and concentration in the feed stream (Lin et al. 2015).

Merkel et al. (2012) considered the cost of CO₂ separation from syngas for a CO₂-selective polymeric membrane. They note that rubbery, CO₂-selective membranes are best operated at low temperatures to optimise CO₂/H₂ selectivity; thus, they estimated the cost of a process with CO₂ separation at 10 °C. A refrigeration process is then used for final purification of the CO₂. The bulk of the H₂S is assumed to end up in the liquid CO₂ for co-sequestration. A membrane area of 16,000 m² is required, with total plant cost estimated at roughly half that of an IGCC process using Selexol. This results in an LCOE for 90% capture roughly 20% higher than the standard IGCC process without CO₂ capture (compared with a 30% increase estimated for Selexol).

5.2.3 Other membrane processes

Additional efficiency gains are anticipated if the membrane is combined with CO₂ removal via adsorption, or the WGS stages of the IGCC process, as membrane reactors. Similar to PCC applications, the use of membranes in a membrane contactor has also been evaluated for IGCC conditions.

Scholes et al. (2012) evaluated a membrane gas-solvent contactor for CO₂ removal from syngas. Two contactors (polypropylene and polytetrafluoroethylene) were evaluated with two solvents (30 wt% MEA and 30 wt% K₂CO₃). Contactors were evaluated in the laboratory, treating a mixture of 10% CO₂ in N₂, and at pilot scale, treating an unshifted syngas from an air-blown gasifier. Mass-transfer coefficients improved with solvent applied to the shell side of the contactor. Pilot-plant trials treating syngas had reduced performance for some contactors due to pore wetting. The polytetrafluoroethylene contactor with 30 wt% MEA provided the best overall mass-transfer coefficient, consistent with literature expectations. Improved process control to minimise pressure differential spikes was important in minimising pore wetting.

The Università degli Studi di Genova have evaluated high pressure (up to 16 bar) membrane contactors at pilot scale, treating gas streams from a refinery and a coke plant. Unloaded solutions of PZ/K₂CO₃ and PZ/MDEA blends were evaluated. Operation under high pressure was noted to improve CO₂ absorption flux. The trans-membrane pressure however had to be carefully controlled to avoid pore wetting (Comite et al. 2017)

The University of Southern California and Media and Process Technologies have evaluated a combined membrane and adsorption reactor. The process uses a carbon molecular-sieve-based H₂ separation membrane, coupled with an adsorption-enhanced WGS reactor (with commercial WGS catalyst in both reactors). This allows for in-situ H₂ permeation and simultaneous CO₂ adsorption

using a hydrotalcite-based adsorbent. The simultaneous removal of H₂ and CO₂ is anticipated to enhance reactor yield and selectivity. The membrane reactor and adsorptive reactor operate in tandem until the adsorbent is saturated, at which time it is regenerated via a TSA process. The use of TSA allows for the recovery of CO₂ at higher pressures, requiring no additional recompression of the CO₂ for storage. H₂ permeating through the membrane can be used in the gas turbine. The H₂ leaving the adsorption reactor is of high purity, and has multiple uses. The membranes used in this process have previously been evaluated at the NCCC. The combined system has undergone laboratory evaluation treating a synthetic syngas. Preliminary techno-economic analysis suggests 90% CO₂ capture is achievable with lower efficiency penalty compared with a standard system using a two-stage Selexol process. A total COE of 51.4 \$/MWh is estimated for the combined membrane and adsorption reactor process (compared with 135.4 \$/MWh for IGCC with Selexol, DOE case B5B) (Tsotis et al. 2017, Chen et al. 2018).

Franz et al. (2014) noted that combining the CO₂-separation membrane with the WGS reaction step reduced the efficiency penalty compared with a system where the steps were completed separately. This led to an efficiency penalty from the addition of 90% CO₂ capture to an IGCC plant of 6% (compared with 8.6% penalty for process with separate steps). The WGS–membrane process saw an efficiency decrease from 47.4% (LHV) to 40.8% (37.1% for Selexol). A membrane area of 69,100 m² was required. With an assumed membrane cost of cost of 300 €/m², COE increased from 45.3 €/MWh for the reference IGCC process to 54.4 €/MWh (57.7 €/MWh for Selexol). At a CO₂ price of 15 €/tCO₂, the WGS membrane reactor becomes economically attractive compared with an IGCC plant without CO₂ capture.

Maas et al. (2016) estimated the cost of CO₂ capture from syngas using a microporous ceramic membrane. They compared two scenarios: the membrane and WGS reactions as separate process steps, and as a combined WGS–membrane reactor. The lowest cost and highest efficiency was determined for the case where the membrane was incorporated with the WGS reactor. This incurred an efficiency penalty of 6.8 percentage points, and had a specific investment cost (2660 €/kW) 33% above the specific investment cost of the reference IGCC plant without carbon capture. For the economic optimum, 63,000-m² membrane was required (membrane price 500 €/m² assumed). The LCOE of the reference IGCC plant was calculated to be 61.5 €/MWh. This increased to 80.6 €/MWh for the plant incorporating the WGS–membrane reactor (30% increase in LCOE, cost of CO₂ avoided 30.5 €/tCO₂). They noted that as the microporous membrane was still under development, it was difficult to set a definite price for the technology and associated components. In addition, the challenge for this process was the development of a steam-tolerant ceramic membrane.

Discussion on commercialisation potential and development since previous review

Based on NCCC and other pilot-scale evaluation, the previous review evaluated H₂ separation membranes as being at a TRL of 5. Since then, additional membranes have been evaluated at similar scale, suggesting the TRL is still at 5–6. With the evaluation completed by MTR in particular, CO₂ separation membranes are similarly at a TRL of 5–6.

The most developed and evaluated membranes are Pd and polymeric H₂-separation membranes. Significant cost reductions are also anticipated when the membranes are combined with other process steps into membrane reactors. These still require long-duration evaluation under relevant process conditions to provide information on real lifetimes.

5.3 Adsorbents

Adsorbents for pre-combustion capture applications involve adsorbing CO₂ into the adsorbent. Large-scale use of CO₂ sorbents is already achieved commercially, particularly for the production of high-purity H₂ from natural-gas reformers. Adsorbents that show an affinity for CO₂ include zeolites, activated carbon, inorganic oxides, amine modified silicates and MOFs (Sun et al. 2015). However, many adsorbents are unstable, or have degraded performance in the presence of H₂O or acidic gases such as H₂S (Yang et al. 2017). One of the major benefits of a PSA process is the potential to carry out CO₂ removal at temperatures higher than used in liquid-absorbent-based processes. This has the potential for improving overall efficiencies by minimising cooling and heating requirements, and the potential of supplying a high-temperature H₂ stream to the gas turbine. Simulation of an IGCC process incorporating CO₂ separation via PSA showed that no advantage was achieved over a liquid-absorption process if a cold PSA process was used (Riboldi et al. 2015). Another advantage of adsorption processes is the potential for CO₂ production at higher pressures. The higher partial pressures of CO₂ in pre-combustion capture render the weakly CO₂-binding physisorbents much more effective than in post-combustion conditions, allowing for efficient PSA with high CO₂ loadings (Lockwood 2016).

Previously, the focus of PSA processes has been on the production of high-purity H₂. For CCS applications, however, high purity and yield of CO₂ is required, causing the cycle design to differ significantly from conventional H₂ PSA (Jansen et al. 2015). Large-scale demonstration of CO₂ sorbents has been achieved by Air Products at the Valero Refinery, Port Arthur, Texas. A CO₂-sorption step was added to the existing VPSA process used to purify H₂ from steam methane reformers. The approximately 1 million tons of CO₂ per year is then used for EOR applications (Baade et al. 2012).

A range of solid sorbents have been investigated at laboratory scale for the purification of H₂ and CO₂ from gasifier syngas. To reduce cost, sorbents derived from waste materials have been considered. Heriot–Watt University have evaluated a fly-ash-derived, lithium-silicate material for the removal of CO₂ from a simulated syngas mixture (Sana et al. 2017). TiO₂ has also been evaluated as a potential low-cost CO₂ sorbent, showing good stability and regenerability (Kensari et al. 2013)

Nanyang Technological University have investigated triphenylamine-containing microporous organic copolymers as a CO₂ adsorbent that is stable under humid conditions. These were evaluated at laboratory scale, and compared with a commercial MOF (HKUST-1) and activated carbon. The triphenylamine adsorbents were found to have a similar CO₂ uptake as the commercial adsorbents (5 mmolCO₂/g sorbent at 10 bar); however, unlike the commercial MOF, the triphenylamine adsorbent was able to maintain CO₂ adsorption capacity under humid conditions (Yang et al. 2017).

Imperial College synthesised hydrotalcite hybrids (Mg/Al ratios varying from 0.3 to 3) to improve stability, absorption capacity and kinetics of the CO₂-capture sorbent. The HT/SBA15 hybrids showed improvement in intrinsic CO₂ uptake, initial uptake rate, and multicycle stability compared with unsupported hydrotalcite (Peng et al. 2018).

Activated-carbon beads, suitable for use in CFBs, have been evaluated by the University of Nottingham. Different post-treatments, including HNO₃ oxidation and subsequent amination at elevated temperatures, were evaluated and found to improve performance by 20% (Sun et al. 2013, 2015, Caldwell et al. 2015). Phenol–formaldehyde, resin-derived, activated carbons have also been

evaluated by INCAR-CSIC, with sorbent regeneration via PSA and PTSA processes. While the latter process proved to be more effective, higher temperatures were noted to decrease product purity (Garcia et al. 2013). MIT evaluated MgO-impregnated activated carbons for warm CO₂ capture via PSA (180–240 °C). The sorbent was observed to perform better than a synthetic and K₂CO₃ promoted hydrotalcite (Liu and Green 2013)

The National Polytechnic Institute, Mexico, evaluated several zeolite-like imidazolate frameworks for separation of CO₂–H₂ mixtures. These structures are reported to have high CO₂ sorption capabilities while maintaining structural stability in the presence of water vapour (Samano-Alonso et al. 2016).

While a significant amount of research has been completed at laboratory scale for pre-combustion separation of CO₂ via solid-sorbent processes, a few have proceeded to pilot-scale evaluation. Some of the technologies that have progressed to pilot-scale evaluation are summarised in Table 35.

Table 35 Adsorbents evaluated at pilot scale for pre-combustion capture

TECHNOLOGY COMPANY/RESEARCH INSTITUTE	DESCRIPTION	COST AND ENERGY INFORMATION	REFERENCES
Mesoporous carbon modified with functional groups TDA	Removes CO ₂ via strong physical adsorption under pre-combustion capture conditions. CO ₂ –surface interaction is strong enough to allow operation at higher temperatures, while still maintaining low regeneration-energy requirement. Sorbent regenerated via combined pressure and concentration swing. Pilot-scale evaluation (0.1 MW _e) at National Carbon Capture Centre (NCCC) facility using 2 m ³ of adsorbent. 700 h of operation with CO ₂ capture efficiencies above 90%. Further evaluation treating slipstream from O ₂ -blown gasifier to be achieved at Sinopec in 2018.	Energy requirement for sorbent regeneration is claimed similar to Selexol; however, as capture can be completed at higher temperature, achieves higher overall efficiency. Techno-economic analysis suggests efficiency and cost of electricity (COE) improvement over same facility using Selexol process. Cost of CO ₂ capture \$30–31/tonne CO ₂ captured, compared with \$37–43/tonne for Selexol (GE and E-gas gasifiers).	Alptekin et al. 2017
Zeolites 13X CO2CRC	Zeolite adsorbents 13X evaluated for CO ₂ capture from an unshifted syngas from a pilot-scale air-blown gasifier. Zeolite 3A was applied at either end of the reactor to protect the CO ₂ sorbent from moisture. A range of vacuum pressure-swing adsorption (VPSA) processes was evaluated. CO ₂ capture between 70–88% achieved with CO ₂ concentrations in the range 70–98%, depending on the regeneration process used.		Anderson et al. 2011
Sour PSA Air Products	Air Products have evaluated a two-stage PSA process for removing CO ₂ and H ₂ S from gasifier syngas. This includes a tailgas disposition block that separates the sulfur-containing compounds and purifies the CO ₂ to a sequestration-grade product. This process was evaluated at pilot scale on Energy and Environmental Research Centre’s oxygen-blown fluidised-bed gasifier.	A preliminary techno-economic assessment suggests a COE for a gasification process incorporating the sour PSA process and Claus Unit of 117 \$/MWh, a reduction from the 122 \$/MWh predicted for the base case incorporating a Selexol process.	Kloosterman 2012

5.3.1 Sorbent-enhanced water-gas shift

Combining adsorption-based CO₂ removal with the WGS unit is known as the sorption-enhanced WGS process (SEWGS). This process allows an increase in the conversion of CO due to the removal of one of the products (CO₂) by the sorbent. The steam consumption in the WGS section contributes significantly to the CO₂-capture penalty. This can be minimised using the SEWGS process (Jansen et al. 2015, Torreiro et al. 2017). Rather than using two separate reactors for the WGS process (high-temperature shift and low-temperature shift reactors), the SEWGS process either replaces the low-temperature shift, or uses a single reactor operating at high temperature, minimising the energy penalty associated with the cooling step between the reactors. WGS catalysts to be used in a SEWGS process should be highly active at temperatures in the range of 300–500 °C, show resistance to sintering at temperatures above 450–500 °C and maintain a stable performance under cyclic operating conditions (Marono et al. 2014). Suitable sorbents should have a high CO₂-capture capacity and selectivity towards CO₂ at temperatures in the range of 300–500 °C, adequate sorption–desorption kinetics (easily regenerable), mechanical strength and low cost. Typically, potassium-promoted, hydrotalcite-based materials are used. These materials have excellent hydrothermal stability, are active for the WGS reaction, are robust to H₂S and can be operated with a low steam feed (Jansen et al. 2015). In addition, calcium oxide, Na₂O-modified alumina, modified MgO, and alkali metal zirconate materials have been evaluated for SEWGS (Lee and Lee 2017)

Najmi et al. (2014) completed a dynamic simulation of an IGCC plant with a SEWGS unit and gas turbine. They found that the SEWGS unit was much less responsive to load changes than the gas turbine, potentially reducing operational flexibility of the IGCC plant. They suggested adding an intermediate buffer tank to improve process flexibility.

Korea Electric Power Research Institute evaluated five MgO-based CO₂ sorbents and five Cu-based WGS catalysts for fluidised-bed-based SEWGS. Sorbent and catalyst particles were prepared via spray drying, and found to have attrition rates between 10 and 15% when subjected to fluidised-bed conditions (Lee et al. 2011). CO₂-sorption capacities (3–14 wt%) were evaluated in a bench-scale, pressurised, bubbling fluidised bed (Choi et al. 2013). CO₂ sorption capacity was also noted to increase when steam treatment was applied.

Korea University evaluated a Na–Mg double salt sorbent for CO₂ capture from syngas. The double salt sorbent is reported to have a high sorption capacity and fast kinetics. However, SEWGS experiments with a one-body hybrid solid prepared by combination with a commercial WGS catalyst showed poor reactivity and reduced CO₂ uptake. To overcome this, a divided packing concept was proposed to separate the catalyst and CO₂ sorbent. Separate layers of catalyst and sorbent particles were placed alternately in the reactor. This allowed a high-purity H₂ stream (<10 ppm CO) to be produced from their laboratory-scale, fixed-bed experiments (Lee and Lee 2017).

Southeast University, China, evaluated a CaO–MgO molecular sieve sorbent for 20 absorption–desorption cycles in a TGA. H₂ yields were noted to increase for the modified sorbent compared with untreated CaO (Sun et al. 2016).

CIEMAT, Spain, evaluated two hydrotalcite catalysts for the removal of CO₂ and H₂S from synthetic gas mixtures in a laboratory-scale fixed-bed reactor. Competition between adsorption of CO₂ and H₂S was observed (Torreiro et al. 2017).

Evaluation of SEWGS processes has progressed to pilot-scale evaluation, often treating a slipstream of syngas from a coal-based gasification process. A summary of research in this area that has reached pilot-scale evaluation is summarised in Table 36.

Table 36 Pilot-scale evaluation of sorption-enhanced water–gas shift (SEWGS) process

TECHNOLOGY COMPANY/RESEARCH INSTITUTE	DESCRIPTION	COST AND ENERGY INFORMATION	REFERENCES
P-110 Korea Institute of Energy Research	CO ₂ absorbent mixed with commercial water–gas shift (WGS) catalyst (ratio 1 sorbent:3 catalyst) evaluated on 1 Nm ³ /hr slipstream from pilot-scale gasifier. The SEWGS reactor was downstream of filtration and desulfurisation units, and consisted of bubbling fluidised-bed reactors. SEWGS process operated at 18 bar and 236 °C, with regeneration of the sorbent at 350 °C. Continuous operation for 50 hours was achieved with sulfur capture efficiency of 99.6%, CO conversion of 98.9% and CO ₂ capture efficiency of 98% achieved.		Ryu et al. 2017
Combined sorbent- based CO ₂ capture WGS reactor Southern Research IntraMicron Nexant	Process is designed to operate at warm gas temperatures, reducing parasitic energy losses. The process also makes use of IntraMicron’s microfibrus entrapped catalyst technology. The MgO-based CO ₂ capture sorbent is currently undergoing laboratory-scale evaluation. Aim of the project is to progress the technology through to a TRL of 5.	Preliminary techno-economic assessment suggests the combined CO ₂ -capture/WGS microfibrus entrapped catalyst reactor reduced the capital cost of the gas clean-up section of an IGCC by 20%.	Gangwal and Zhao 2018
URS University of Illinois at Urbana- Champaign	Process simulation and sorbent molecular and thermodynamic analysis used to identify sorbent materials for a combined WGS-CO ₂ capture process. The goal of the project was to identify sorbents able to achieve 90% CO ₂ capture with high loading capacities, and operate at the high temperature and pressures encountered in a WGS reactor. Completing CO ₂ capture at high temperature and pressure anticipated to minimise energy-efficiency impacts on the IGCC process. Four nano-engineered sorbents were selected for further evaluation, with capacities approaching 0.4 gCO ₂ /g sorbent. No significant impacts of H ₂ S observed. Techno-economic assessment of standard process showed minimal benefit over base case. A more technically challenging approach was found to be economically competitive; however, technical challenges still remain.	A CaO absorbent was identified for further assessment. Based on laboratory results, a techno-economic assessment was completed in Aspen. A slipstream of the product H ₂ is used to provide the heat for CaO regeneration. Five different process cases were investigated, with all achieving higher overall efficiencies than a standard IGCC process with CO ₂ capture. The optimal SEWGS case has a cost of electricity (COE) of 97.50 \$/MWh compared with 119.40 \$/MWh for IGCC with standard CO ₂ capture process.	Richardson 2013 Steen et al. 2014
ALKASORB+ ECN PTM SINTEF Air Products BP	K ₂ CO ₃ promoted hydrotalcite-based compound. Able to capture both CO ₂ and H ₂ S from gas stream without significant loss of capacity. Able to achieve complete CO conversion without separate WGS catalyst. CO ₂ absorption completed at 350–550 °C, increasing efficiency by minimising cooling/re-heating requirements. Continuous process demonstrated in test rig using five parallel reactors (6 m in length, 25 kg sorbent) treating a synthetic gas stream (25 kW _{th} scale). Sorbent remained chemically and mechanically stable after 2000 absorption–desorption cycles. Classified at TRL 5–6 using NASA’s TRL scale.	Cost of CO ₂ avoided 23 €/t (40% reduction compared with Selexol). Specific energy consumption 2.08 MJ (LHV)/kgCO ₂ (Selexol 3.71 MJ/kgCO ₂). COE 82.3 €/MWh (89.6 €/MWh for Selexol based process).	Jansen et al. 2013 van Selow et al. 2013 van Dijk et al. 2017 CAESAR 2011

TECHNOLOGY COMPANY/RESEARCH INSTITUTE	DESCRIPTION	COST AND ENERGY INFORMATION	REFERENCES
	This project is being progressed to pilot-scale evaluation (14 t/d) at a blast furnace site through the EU STEPWISE project. The pilot-scale evaluation will progress the technology through to a TRL of 6.		

5.3.2 Ca-looping enhanced H₂ production in the water gas shift reaction

As with PCC, Ca-looping processes can be applied to CO₂ removal from syngas. As the CaO reacts with CO₂ in the syngas, forming CaCO₃, the CO₂ is removed from the gas stream, promoting additional H₂ generation via the WGS reaction. This potentially removes the requirement for adding WGS catalysts, and can lower the steam requirement of the shift process. In addition to capturing CO₂, the CaO reacts with other acid gases (i.e. hydrogen sulfide (H₂S), carbonyl sulfide (COS), and hydrogen chloride (HCl)) to form solid products. The heat produced in the carbonation reactor can be used to raise additional steam (Connell et al. 2013, Phalak et al. 2012).

CanmetENERGY have evaluated this process at pilot scale, under batch operation, treating a synthetic feed gas mixture. An increase in carbonation conversion was observed when simulated syngas conditions were used as opposed to carbonation with CO₂ only. Analysis of the outlet gases confirmed that the calcined limestone catalysed the WGS reaction. This is thought to enhance CO₂ concentration levels at the grain surfaces of the sorbent (Symonds et al. 2009).

Ohio State University evaluated Ca looping for the removal of CO₂ from a N₂/CO mix. They note that the Ca-based sorbent is able to remove CO₂, sulfur and halide impurities from the syngas in a single process step. They investigated the optimum conditions for H₂ production in the absence of a WGS catalyst using a laboratory-scale, fixed-bed reactor. They were able to obtain high pressures, high CO conversion and high H₂ purity (>99%) in the absence of a WGS catalyst at near-stoichiometric steam:carbon ratios (Ramkumar and Fan 2010). As an extension of this work, Connell et al. (2013) simulated a Ca-looping process for the removal of CO₂ from a coal-to-H₂ plant, steam methane reforming and IGCC using Aspen Plus. They included a hydration step between the calcination and carbonation steps for sorbent reactivation. Each technology was compared against a base-case system, using a two-stage Selexol process for H₂S and CO₂ removal. Due to the co-absorption of other acid gases present in the syngas (e.g. H₂S, HCl), some of the pre-treatment steps used in the base-case technologies were no longer required in the Ca-looping processes. In all cases, the Ca-looping processes required more O₂ and coal than the base case. This was required for sorbent regeneration in the calciner. Energy recovery in the Ca-looping process, however, allowed for the production of additional steam and electricity. For the IGCC case, the Ca-looping process was found to be more efficient than the base-case technology (33.1 c.f. 32.7% overall efficiency, HHV). For all cases, the Ca-looping process achieved 9–12% lower first-year cost of H₂, or first-year COE, compared with the base-case technology. For the IGCC case, first-year COE was estimated to be \$90.7/MWh (c.f. \$103/MWh for the base case). The authors note that at the time of writing, the principal technical uncertainties included the performance of the high-temperature hydrator with internal heat recovery, which had not yet been demonstrated, and the use of oxycombustion in the coal-fired flash calciner, which represents a new mode of operation for these technologies. Continuing the laboratory-scale demonstration of Ca-looping, researchers at Ohio State University developed a sub-pilot-scale, fluidised-bed carbonator. As the full Ca-looping process will include

a hydration step to reactivate spent sorbent, $\text{Ca}(\text{OH})_2$ was fed to the carbonator. As the $\text{Ca}(\text{OH})_2$ decomposes to CaO , the H_2O released is able to replace some of the steam requirement. Experiments conducted using a synthetic syngas were able to achieve complete CO_2 capture, and produced a product gas containing 70% H_2 . The performance of the sub-pilot, fluidised-bed reactor was slightly poorer than that of the laboratory-scale fixed-bed reactor, thought to be due to better gas–solid contact and Ca:C ratio in the laboratory reactor (Phalak et al. 2012).

Researchers at the University of Stuttgart evaluated at 20-kW_{th} dual-fluidised-bed facility for CO_2 removal from a synthetic syngas. A H_2 concentration of 84.4 vol% dry, and a CO_2 conversion of 76.4% were achieved with a carbonator temperature of 639 °C, a looping ratio of 6 mol Ca/mol CO+ CO_2 and a space time of 1 h. A 150-mm diameter, bubbling fluidised bed was used for the carbonator, and a 70-mm diameter, 12.4-m high CFB was used for the calciner. CO_2 capture efficiencies above 90% were achieved; however, CO conversion was found to be low, indicating that the kinetics of the WGS reaction are relatively slow without a catalyst present in the temperature range investigated (~650 °C). Attrition of the sorbent was evaluated by measuring material loss during the operation, and found to be 1.7 wt% of the total system inventory per hour of operation. For all syngas compositions evaluated, H_2 concentrations >70 vol% dry and CO conversion >70% were achieved. Comparison to literature data for gasification systems using two-stage WGS reactors suggests that the Ca-looping process is able to achieve comparable, or even higher, H_2 concentrations. The authors note, however, that for the experiments completed here, a synthetic syngas was used, and hence the effect of tars and other impurities on the process is not yet fully understood (Armbrust et al. 2015).

Connell et al. (2013) note that additional research is required to resolve technical uncertainties related to the commercial application of the Ca-looping technology applied to syngas treatment. This includes evaluation of sulfur chemistry in the oxy-fired calciner, development and demonstration of the high-temperature hydrator with internal heat recovery, evaluation of the carbonator performance at larger scale and wider range of operating conditions, evaluation of cyclone performance with very high solids loadings and small particle sizes, and demonstration of solids handling in the integrated process at relevant scale.

5.3.3 Sorbent-enhanced reforming/gasification

In sorbent-enhanced reforming, hydrocarbon reforming, water gas shift, and CO_2 separation occur in a single reaction step over a reforming catalyst mixed with a CO_2 sorbent. This enhances H_2 production from the water gas shift reaction, and can result in H_2 concentrations up to 98% (dry basis). CO_2 sorbents evaluated for this process include Ca-based oxides, K-promoted hydrotalcite and mixed metal oxides of lithium and sodium (Harrison 2008). Sorbent-enhanced gasification is a similar concept, with the gasification reactions carried out in the same reactor as the CO_2 sorption.

Sorption enhanced reforming has been explored as part of the Zero Emission Gas Power Project, with H_2 produced to be used in fuel cells. Sorption-enhanced reforming of natural gas was also explored by Pratt and Whitney Rocketdyne. Los Alamos National Laboratory's Zero Emission Carbon project was designed to produce carbon free H_2 and electricity from coal (Harrison 2008).

One of the challenges when using CaO for sorption enhanced reforming is the endothermic CaCO_3 calcination in high CO_2 environments. To solve this, CSIC have proposed the Ca-Cu process, where

the exothermic reduction reaction of CuO with natural gas, CO or H₂ has been shown to provide sufficient heat for the calcination (Fernandez et al. 2012, Abanades et al. 2010). The principle reaction steps in the Ca-Cu process are outlined in Figure 15. CSIC have completed laboratory-scale evaluation of CO₂ sorbents used to enhance H₂ production via steam methane reforming. They developed synthetic CaO-based sorbents showing improved mechanical stability during multi-cycle operation (100 cycles). The sorbent was evaluated with a commercial catalyst under reforming conditions, producing a 92% H₂ (dry basis) stream (Lopez et al. 2017). This has been progressed through the EU-Ascent project, with the complete Ca-Cu cycle evaluated at bench-scale in fixed bed reactors (Diez-Martin et al. 2019). Results proved the ability to perform calcination/reduction and steam methane reforming in a single stage. An optimised design has also been proposed (Fernandez and Abanades 2017). A techno-economic assessment has been completed for a H₂ production plant, and compared to a conventional process using a fired tubular reformer and CO₂ capture by MDEA absorption. The Ca-Cu based process had a hydrogen production cost of 0.178 €/Nm³ and a CO₂ avoided cost of 30.96 €/ton. These costs were found to be respectively 8% and 52% lower than for the conventional process (Riva et al. 2018). Where the produced H₂ is used for power production, an electricity cost of 82.6 €/MWh is suggested for the Ca-Cu based power plant, 2.2 €/MWh below a similar plant using an auto thermal reformer with CO₂ capture via an MDEA absorption process (Martinez et al. 2019).

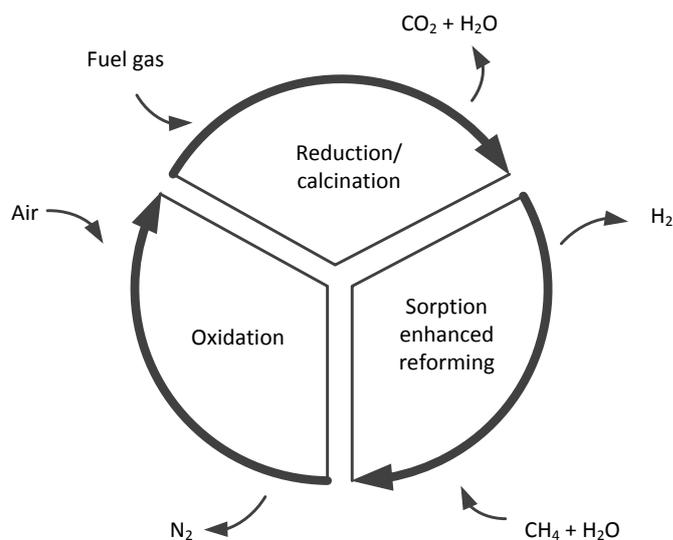


Figure 15 Principle reaction steps in the Ca-Cu process for H₂ production (Fernandez and Abanades 2017)

The HyPr-RING process proposed by JCOAL (Lin et al. 2011) is a novel gasification process combining coal gasification with CO₂ removal using CaO during the gasification process. The formation of CaCO₃ in the gasifier provides heat that can be utilised for the gasification reactions. This has been evaluated in a bench-scale gasifier and calciner.

5.3.4 Hybrid systems

Some researchers have investigated combining SEWGS with a H₂-selective membrane. This allows for the removal of both CO₂ and H₂ simultaneously from the syngas mixture, with potential for added enhancement of the WGS reaction and H₂ production.

Researchers from CIEMAT have evaluated a combined SEWGS and Pd-membrane reactor for pre-combustion CO₂ capture and H₂ production. Their hybrid system consists of a high-capacity CO₂ sorbent (K-doped hydrotalcite), a high-temperature commercial Fe–Cr WGS catalyst, and a dense Pd membrane highly selective for H₂. The system was evaluated at bench scale treating a synthetic syngas mixture. A complete sorption–desorption cycle was typically 3–4 hours. The system was heated to 500 °C during the regeneration steps, which reduced the activity of the catalyst at operating temperatures below 350 °C. They concluded a compromise was required when selecting the process temperature for the catalyst/sorbent system used, with low temperatures favouring CO₂ capture and high temperatures favouring the conversion of CO. They determined operating temperatures in the range 350–375 °C to be an adequate compromise. The presence of the membrane had a positive effect on the catalytic behaviour of the hybrid systems up to CO₂ breakthrough; however, some evidence of the reverse WGS reaction was observed. To avoid this, the use of excess steam was recommended (Marono et al. 2014).

Discussion on commercialisation potential and development since previous review

SEWGS, particularly the ALKASORB process, was evaluated in the previous review. ALKASORB had been evaluated at laboratory pilot scale, and assessed as being at a TRL 5. Since then, TDA's and Korean Institute of Energy Research's sorbents have achieved a similar level of demonstration. Full system evaluation, identified as a requirement in previous review, has still not been achieved. Hence, the TRL is assessed as still being at 5–6.

Since the previous review, progress has also been made in the field of sorption enhanced reforming. The Ca-Cu process in particular has received significant attention, and has now reached a TRL of 4–5 with experimental campaigns completed at CSIC and Eindhoven University of Technology (Martinez et al. 2019b). Ongoing work is expected to focus on improving the mechanical stability of the functioning materials, particularly under shifting temperature, pressure and redox environments.

5.4 Cryogenic separation

As with post-combustion and oxyfuel combustion cases, CO₂ can also be removed from syngas streams via cryogenic distillation. The higher partial pressures of CO₂ in pre-combustion capture applications are more amenable to CO₂ capture via cooling.

The CO₂CRC and Curtin University of Technology proposed a combined cryogenic and hydrate-based separation of CO₂ from syngas. Syngas is cooled (to –55 °C) for initial removal of liquid CO₂. The H₂-rich overhead gas is then passed to a hydrate reactor (operating temperature of 1 °C), where it is contacted with water for additional CO₂ removal by forming a hydrate-in-water slurry. Hysys simulation suggests CO₂ liquid formed in the cooling step is 95% pure. Hydrate from the precipitation can be dissociated to obtain CO₂ at 20–40 bar. However, bench-scale experimental evaluation indicated significant difficulty in achieving hydrate formation (Surovtseva et al. 2011).

Air Liquide has developed the CRYOCAPTTM H₂ process for capturing CO₂ from steam methane reforming plants. The technology uses cryogenic purification to separate CO₂ from PSA off-gas. A H₂-separation membrane is also incorporated into the plant, allowing additional H₂ production. They claim that the system can achieve 97% CO₂ capture, with an increase in H₂ production between 10–15%. Air Liquide have started the first commercial plant using this technology at Port-Jerome,

France, in 2015. The plant produces 47,000 Nm³/h H₂, and 300 t/d food-grade liquid CO₂ (Pichot et al. 2017).

Discussion on commercialisation potential and development since previous review

In the previous review, it was noted that the components required for low-temperature separation are widely available, but not yet demonstrated for pre-combustion capture. As such, the TRL was assessed as 2. While the Air Liquide process treats PSA off-gas (rather than syngas), the demonstration suggests the technology has progressed to a TRL of 5.

6 Technologies anticipated to see impact within the next 5–10 years, and their potential to reduce costs

This section considers those technologies that have reached a TRL of 4–6 (i.e. pilot-scale demonstration) and are anticipated to see wider deployment in the next 5–10 years. The technologies were assessed by several metrics to identify those with a higher likelihood of earlier deployment. The criteria used for this assessment are outlined below.

6.1 Criteria for widespread application of CO₂-capture technologies

The deployment of CO₂-capture technologies is first and foremost dependent on the establishment of a successful business case in which investors and facility owners are able to receive a commercial return. Success in CCS is therefore quite dependent on financial or regulatory mechanisms. However, technologies should be sufficiently de-risked and their durability demonstrated before they become bankable. The economic prospects for widespread application of any CO₂-capture technology are determined by a range of factors. These factors are diverse, and also cover significant non-technical aspects, such as the societal acceptance of CCS and the availability of existing infrastructure. However, they are decisively influenced by the investment and operating cost of any particular technology.

Costs for emerging capture technologies are often difficult to determine with great certainty. Even for leading technologies, such as the amine-based capture processes, the lack of widespread experience on a large scale results in a wide variation in anticipated costs. The costs of ‘first-of-a-kind’ capture technologies are high, as they often constitute a first demonstration of the technology, and sizeable contingencies are applied to ensure a successful demonstration. The resulting added investment costs are the main reason that FOAK plants require government support. Ensuing plants are then assumed to achieve significant cost reductions, as the need for additional contingencies disappears with increasing evidence of reliable operation, as well as plants receiving cost reductions due to ‘learning by doing’ and increasing economies of scale. Combined technology demonstration, and supporting research and development efforts, can accelerate technology development and facilitate deployment.

The initial selection of a particular CO₂-capture technology requires a comprehensive understanding of its TRL and its potential for cost reduction. The following list describes determining factors related to the capture technology and its application in certain markets:

- **Context of application, i.e. power plant or industrial facility.** The expertise available within an industrial sector or at company level can influence the technology adoption. For instance, in applications or industries where there is ample expertise in off-gas treatment, the use of PCC technologies will have lower training requirements. Power-plant operations also increasingly require flexible operations in line with fluctuating electricity demand, which is

not the case for industrial applications. This will set the tone for the type of application that would be most suitable in a particular market.

- **Size of the existing application market for a particular CO₂-separation technology as an indicator of technological maturity.** The oil, gas and petrochemical industries use CO₂-separation processes on an ongoing basis in their commercial operations and have an interest in reducing costs for these technologies while maintaining process reliability. If these technologies can be transferred to applications in a CCS context, this can significantly reduce the threshold for deployment. The prime example here is the use of amine processes or physical absorption processes in natural-gas treatment that can be implemented in pre-combustion processes.
- **Availability of underlying technology components critical for further deployment, e.g. CO₂-capture agents or specialised equipment.** Capture technologies often use materials that reversibly and selectively bind with CO₂, or O₂ in the case of oxyfuel systems. The availability of such materials at low cost will facilitate technology scale-up and deployment.
- **Experience with technology and/or its components in existing non-CCS applications.** Capture processes usually consist of a great deal of equipment. If this equipment is already available with little need for design changes, its use will not pose an obstacle for further development. Instead, attention can focus on the overall plant design, interaction between the different components, and ultimately the optimal integration of these.
- **Current experience in CCS applications.** The successful use of a capture system or its components in CCS will provide considerable confidence that similar systems might work in other CCS applications. The spreading of best practices and dissemination of information from successful projects is likely to catalyse other applications.
- **Available information on reliable CO₂-capture technology costs.** At the lower TRLs, information to underpin cost estimates might be lacking. It is not uncommon for costs to be underestimated for low TRL technologies, because potential issues might not be visible at this stage, given that the technology has not yet been exposed to realistic environments.
- **Ease of retrofit to existing power plants and industrial facilities.** CO₂-capture technologies that do not require large efforts in terms of integration with or modifications to the power plant or industrial facility will have a low barrier to deployment.
- **Number of suppliers and their ability to guarantee processes.** In a market environment, the presence of multiple suppliers will result in the establishment of competitive conditions that naturally lead to lower costs, as end users have the luxury of choice. This also means there is a better chance that the equipment will continue to be available in the future, which is important for operations and maintenance.
- **Good environmental performance.** CCS is a solution to a global environmental issue and should not result in additional environmental burdens.

These factors might also change over time with further technology development and demonstration, and need to be translated into a set of metrics that can be used for the evaluation and qualification of prospective technologies.

6.2 Selection of technologies for further assessment

The selection of technologies for further assessment was based on those that were judged to be at TRL 4–6 and therefore showed promise for potential deployment in PCC applications in the next 5–10 years.

The technologies were assessed based on the information available in accordance with seven different attributes. These reflected the considerations listed in Section 6.1 and are given in Table 37. The attributes were chosen to provide an additional assessment over the TRL classification. All attributes were scored on a scale of 1–3, with the highest possible score being 21. The scores represent the current state of development, and are likely to change (increase) as technologies progress through their development stages.

These technologies, 23 in total, are listed in Table 36. New, amine-based, liquid-absorbent technologies have not been included. While many of these have achieved pilot-scale demonstration (TRL 6 or above), the benefits are expected to be similar to those of current commercial offerings (e.g. from MHI and Shell Cansolv). In addition, evaluation of a generic second-generation liquid absorbent, and its impact on cost reduction compared with the 30 wt% MEA baseline liquid absorbent, is covered in detail in Part II of this report.

Table 37 Technology attributes and scoring description, including advanced, amine-based post-combustion capture (PCC) technologies as an example

ATTRIBUTE	SCORE CLARIFICATION	SCORE FOR ADVANCED, AMINE-BASED PCC TECHNOLOGIES
Level of demonstration achieved and technology readiness level (TRL)	1: Mostly TRL 1–6 2: Mostly TRL 4–6 3: Mostly TRL 7–9 Number of technology suppliers is also taken into account in the analysis: more suppliers → higher score	3: Many technology suppliers
Cost information	1: Expected cost reduction in levelised cost of electricity (LCOE) <10% 2: Expected cost reduction in LCOE between 10 and 30% 3: Expected cost reduction in LCOE >30%	1: Cost reduction of <10% expected compared with MEA (see Part II of this report)
Other applications of the technology	1: No other markets for the technology 2: Niche applications for the technology 3: Applications other than carbon capture and storage (CCS) widespread	3: Amine technology can be widely applied in other applications
Size of existing market	1: Non-existent 2: Limited application, i.e. niche markets 3: Applications existing not for CCS	3: Applications in methanol production, urea production and commercial CO ₂ production
Availability and maturity of technology components; ease of technology supply	1: Significant development in technology components required 2: Some components commercially available, but not all 3: All components available for scale-up	3: Technology has undergone scale-up and is used in two power plants
Ease of retrofit	1: Technology is applied in new installations 2: Significant modifications required to the power plant 3: Essentially an end-of-pipe technology that can be added easily	3: Amine based PCC technology can be retrofitted to power plants

ATTRIBUTE	SCORE CLARIFICATION	SCORE FOR ADVANCED, AMINE-BASED PCC TECHNOLOGIES
Engineering required for CCS/ research & development required	1: Substantial new engineering effort required for large-scale demonstration 2: Some components have been designed and demonstrated for typical applications in CCS 3: Technology has been integrated with a power plant	3: Large-scale integrated plant has been realised
Total	–	19

As an example, amine-based PCC was scored using the attributes in Table 37. This technology scored 19 out 21 points, with only the cost attribute scoring less than 3, as the reduction in LCOE compared with the standard MEA-based process was <10%. This indicates that for a technology to be considered successful, a perfect score is not necessary. However, a technology that would have the same attributes as amine-based PCC but with a lower cost would challenge the strong position of amine-based PCC.

Table 38 Summary and attribute scores of technologies anticipated to see deployment in the next 5–10 years. Results in brackets are values at the time of the previous IEAGHG report (2014)

TECHNOLOGY AND TECHNOLOGY DEVELOPERS	LEVEL OF DEMONSTRATION ACHIEVED AND TECHNOLOGY READINESS LEVEL	COST INFORMATION	OTHER APPLICATION OF TECHNOLOGY	SIZE OF EXISTING MARKET	AVAILABILITY AND MATURITY OF TECHNOLOGY COMPONENTS; EASE OF TECHNOLOGY SUPPLY	EASE OF RETROFIT	ENGINEERING FOR CARBON CAPTURE & STORAGE/RESEARCH & DEVELOPMENT REQUIRED	TOTAL SCORE
Post-combustion capture								
Electrochemical separation FuelCell Energy	2 Pilot, TRL 4, but will increase to 6 after planned pilot-scale demonstration Evaluated at bench-scale treating synthetic flue gases	3 Approx. 31% reduction in cost of electricity (COE) c.f. 30% monoethanolamine (MEA)	3 Standard fuel cells (without the ability to capture CO ₂) have seen scale-up in modular units for power-generating plant up to 60 MW	2 Fuel cells are applied in sizeable but niche markets; not yet competitive in large-scale electricity generation	3 FuelCell Energy shipped first commercial molten carbonate fuel cell in 2003 Today have installed several hundred MW at 50 locations, including a 59-MW combined heat and power plant in Korea	3 High as end-of-pipe technology	2 Demonstration with flue gas from power plants for CO ₂ -separation now occurring Flue gas impurities are cause of concern	18
Solid sorbents–vacuum pressure-swing adsorption (VPSA) and combined temperature and pressure-swing (TPSA) CSIRO East China University of Science and Technology Korea Institute of Energy Research (KIER) National University Singapore TDA	2 Pilot, TRL 6 (3) Slipstream evaluation completed on synthetic and coal power plant flue gas	2 Approx. 17% reduction in COE c.f. 30% MEA	3 Commercially produced zeolites and other adsorbents have been evaluated	2 Solid sorbents are used for a large number of applications, e.g. hydrogen separation, air separation, CO ₂ removal from biogas	3 VPSA systems used commercially in natural-gas processing	3 High as end-of-pipe technology	2 For most sorbents evaluated, vacuum electrical-energy requirement unfavourable compared with current state of the art processes	17
Liquid–liquid separating	2 Small pilot, 4 (4, 6 after planned pilot evaluation)	2 Approx. 9% reduction in LCOE c.f. 30 wt% MEA	3 Liquid–liquid extraction processes will be	1 Non-existent	3 Based on standard liquid - absorbent process,	3 High as end-of-pipe technology	2 For DMX process, evaluation on process gas stream required to	16

TECHNOLOGY AND TECHNOLOGY DEVELOPERS	LEVEL OF DEMONSTRATION ACHIEVED AND TECHNOLOGY READINESS LEVEL	COST INFORMATION	OTHER APPLICATION OF TECHNOLOGY	SIZE OF EXISTING MARKET	AVAILABILITY AND MATURITY OF TECHNOLOGY COMPONENTS; EASE OF TECHNOLOGY SUPPLY	EASE OF RETROFIT	ENGINEERING FOR CARBON CAPTURE & STORAGE/RESEARCH & DEVELOPMENT REQUIRED	TOTAL SCORE
French Petroleum Institute (IFP) Energies Nouvelles (IFPEN) SINTEF/Norwegian University of Science and Technology (NTNU)	Evaluation on synthetic flue-gas streams	(16% reduction in LCOE c.f. 30% MEA estimated)	relevant to this technology; other applications similar to that for amine-based processes		components commercially available Decanting technologies already used commercially in other applications		determine information on degradation rates and emissions SINTEF process has challenges with absorbent volatility	
Non-aqueous (water-lean) and non-amine absorbents GE RTI International C-Capture	2 Pilot, 4–6 Slipstream evaluations completed on biomass and coal power plant flue gas	2 Where cost information available, 10–12% reduction in COE c.f. 30 wt% MEA estimated	3 Some diluents are suitable physical absorbents and could be used for that purpose; similar to that for amine-based processes	1 Non-existent	3 Based on standard liquid-absorbent process, components commercially available	3 High as end-of-pipe technology	2 Solvent stability issues need to be addressed for GE process Limited public information available for C-Capture process RTI proceeding to demonstration project	16
Amino-acid and mixed-salt processes Siemens SRI International Netherlands Organisation for Applied Scientific Research (TNO)	2 Pilot, 4–6 Slipstream evaluation completed on synthetic and coal power plant flue gas	1 8.4% reduction in COE c.f. 30 wt% MEA suggested for SRI International process	3 Some components have already been applied for gas treatment Similar to that for amine-based processes	2 Small-scale applications based on Alkazid process	3 Based on standard liquid-absorbent process, components commercially available Due to low volatility, amino-acid process requires non-standard process for absorbent reclamation Low degradation rates anticipated to ease demonstration requirements	3 High as end-of-pipe technology	2 Siemens are not currently developing this technology while they wait for market opportunities to develop For TNO process, oxidation rate of model amino acid found to be rate limiting. Requires pilot-scale evaluation of complete process SRI proceeding to demonstration project	16
Solid sorbents–TSA Inventys ADA-ES	2 Pilot, 6 (1) Slipstream evaluation	2 Approx. 0–20.2% reduction in COE c.f. 30% MEA	2	2 Solid sorbents are used for applications, such as VOC-removal; large	3	3	2	16

TECHNOLOGY AND TECHNOLOGY DEVELOPERS	LEVEL OF DEMONSTRATION ACHIEVED AND TECHNOLOGY READINESS LEVEL	COST INFORMATION	OTHER APPLICATION OF TECHNOLOGY	SIZE OF EXISTING MARKET	AVAILABILITY AND MATURITY OF TECHNOLOGY COMPONENTS; EASE OF TECHNOLOGY SUPPLY	EASE OF RETROFIT	ENGINEERING FOR CARBON CAPTURE & STORAGE/RESEARCH & DEVELOPMENT REQUIRED	TOTAL SCORE
Kawasaki Heavy Industries (KHI) SRI International Research Triangle Institute (RTI) International TDA Research KIER	completed on coal power and cement plant flue gas		Technology is specific to flue-gas treatment but can be used for other gas treatment processes KHI sorbent modified from commercial product used for CO ₂ removal from air	volume by small amounts recovered	Inventys uses sorbent from commercial suppliers (fabricated into structured beds by Inventys); rotary air pre-heaters commercially available SRI and RTI sorbents have seen some scale-up by commercial manufacturer KHI sorbent used commercially in other applications KIER sorbent produced by commercial supplier	High as end-of-pipe technology. Components available at required scale KHI process uses waste heat for regeneration. Most processes used fluidised beds for regeneration	Inventys processes has seen issues with leakage of sealing valves under vacuum conditions that could potentially be problem for scale-up KHI and SRI processes use novel moving bed contactor Long-term evaluation on process gas stream required to confirm sorbent stability	
Catalysts and other activators Novozymes Technical University of Denmark CO ₂ Solutions	2 Pilot, 3–6 (1) Slipstream evaluation completed on synthetic, NGCC and coal power plant flue gas	2 9–15% reduction in COE c.f. 30 wt% MEA estimated	2 Enzymes are being used on large scale for a range of diverse applications	1 Non-existent	3 Based on standard liquid-absorbent process, components commercially available Industrial-scale production of enzymes already established in other industries	3 High as end-of-pipe technology	2 Akermin no longer progressing technology. Assets sold to CO ₂ Solutions. Novozymes had issues with enzyme longevity. Enzyme not able to withstand typical regeneration temperatures. CO ₂ Solutions proceeding to commercial demonstration	15
Precipitating process UNO Technology TNO Shell GE CarbonOrO SINTEF	2 Pilot, 4–6 (4–5) Slipstream evaluation completed on biogas, synthetic and coal power	2 Where cost information is available, reductions in LCOE of 0–28% estimated c.f. 30 wt% MEA	3	1 Non-existent	2 Based on standard liquid-absorbent process, components commercially available For chilled ammonia process (CAP), chilling	3 High as end-of-pipe technology. For processes employing K ₂ CO ₃ , limited degradation expected for absorbent	1 Challenges dealing with precipitation in process designed for liquid absorbents. For K ₂ CO ₃ processes, different process to that used in natural-gas upgrading. For CAP, benefit of	14

TECHNOLOGY AND TECHNOLOGY DEVELOPERS	LEVEL OF DEMONSTRATION ACHIEVED AND TECHNOLOGY READINESS LEVEL	COST INFORMATION	OTHER APPLICATION OF TECHNOLOGY	SIZE OF EXISTING MARKET	AVAILABILITY AND MATURITY OF TECHNOLOGY COMPONENTS; EASE OF TECHNOLOGY SUPPLY	EASE OF RETROFIT	ENGINEERING FOR CARBON CAPTURE & STORAGE/RESEARCH & DEVELOPMENT REQUIRED	TOTAL SCORE
	plant flue-gas streams	Note: cost information completed for 90% capture. This is yet to be demonstrated at pilot scale	Similar to that for amine-based processes; precipitating processes widely used in the minerals industry Non-precipitating K ₂ CO ₃ process used in natural-gas upgrading		technology required commercially available SINTEF process considering using novel froth contactor that requires demonstration in application		precipitation offset by additional chilling requirements and operational challenges. Company no longer pursuing precipitating process. Limited public information for CarbonOrO process. For SINTEF process, evaluation on process gas stream required to determine information on degradation rates and emissions. Evaluation of novel contactor also required	
Membranes	2	1	3	2	2	2	2	14
Membrane Technology and Research Inc. (MTR) Helmholtz-Zentrum Geesthacht NTNU/SINTEF Ohio State University	Pilot, 5–6 (6) Slipstream evaluation completed on coal power plant flue gas	4–10% reduction in COE c.f. 30 wt% MEA (at 90% capture) Note: membrane processes have shown improved economics at capture rates below 90%	Membranes can be used for other gas-treatment applications	Current \$2 billion in natural-gas treatment, relatively small scale	Mature except for membrane modules Large-scale membrane production applied in other industries (reverse osmosis) Pumping and vacuum equipment available at scale required	Medium for MTR process as requires modification of coal-boiler gas flow paths.	Currently limited experience integrating several membrane modules in flue-gas streams with vacuum	
Membrane contactors and hybrid membrane processes	2	2	3	1	2	3	1	14
Air Liquide Gas Technology Institute (GTI) MTR-TDA	Pilot, 6 (6) Slipstream evaluation completed on coal power plant flue gas	15–20% reduction in COE anticipated c.f. 30% MEA	Membrane contactors used in degassing of liquids and gas transfer. For CO ₂ -removal smaller-scale applications are possible	Membrane-contactor market is a small subset of the overall membrane market	Mature except for membrane modules Large-scale membrane production applied in other industries (reverse osmosis)	High if applied as end-of-pipe technology. Potentially easier than other membrane technologies as fewer units required.	Currently limited experience integrating several membrane modules in flue-gas streams with vacuum	

TECHNOLOGY AND TECHNOLOGY DEVELOPERS	LEVEL OF DEMONSTRATION ACHIEVED AND TECHNOLOGY READINESS LEVEL	COST INFORMATION	OTHER APPLICATION OF TECHNOLOGY	SIZE OF EXISTING MARKET	AVAILABILITY AND MATURITY OF TECHNOLOGY COMPONENTS; EASE OF TECHNOLOGY SUPPLY	EASE OF RETROFIT	ENGINEERING FOR CARBON CAPTURE & STORAGE/RESEARCH & DEVELOPMENT REQUIRED	TOTAL SCORE
					<p>Pumping and vacuum equipment available at scale required</p> <p>Cooling/refrigeration systems (as required for Air Liquide process) commercially available; fewer units required</p> <p>Membrane contactors used in other industries, but exposure to flue gas and amines limited</p>	Medium for TDA-MTR process as requires modification of coal-boiler gas flow paths (boiler air used for sorbent regeneration)		
Cooling processes	2	2	3	1	2	3	1	14
Sustainable Energy Solutions	Small pilot, 5 (3) Slipstream evaluation from multiple sources	Approx. 20% reduction in LCOE c.f. 30% MEA	Derived from conventional refrigeration systems	Similar to current CO ₂ -liquefaction processes	Equipment required consists largely of refrigeration systems and heat exchangers, which are already commercially available	High as end-of-pipe technology	Long-term evaluation required to demonstrate operability, particularly with slurry processes and self-cleaning heat exchanger. Current Department of Energy project aimed at improving reliability	
Ionic liquids	1	2	3	2	1	3	0	12
ION Engineering	Pilot, 4 (1)	37% increase in cost of electricity over non-capture plant. Approx. 22.6% lower COE c.f. 30 wt% MEA	Ionic liquids have only received limited application for gas treatment; similar to that for amine-based processes; dehydration of gas streams; absorption heat pumps	Applied in Hg-removal from natural gas	Based on standard liquid-absorbent process, components commercially available but costly	High as end-of-pipe technology	Degradation of ionic liquid in presence of amine. Technology no longer being pursued by company	

TECHNOLOGY AND TECHNOLOGY DEVELOPERS	LEVEL OF DEMONSTRATION ACHIEVED AND TECHNOLOGY READINESS LEVEL	COST INFORMATION	OTHER APPLICATION OF TECHNOLOGY	SIZE OF EXISTING MARKET	AVAILABILITY AND MATURITY OF TECHNOLOGY COMPONENTS; EASE OF TECHNOLOGY SUPPLY	EASE OF RETROFIT	ENGINEERING FOR CARBON CAPTURE & STORAGE/RESEARCH & DEVELOPMENT REQUIRED	TOTAL SCORE
High-temperature solid looping processes								
Ca-looping processes	2	2	3	2	3	3	2	17
Spanish research council Hunosa Endesa generacion Foster Wheeler Technical University of Darmstadt Industrial Technology Research Institute University of Stuttgart CanmetENERGY Ohio State University Calix Limited Alstom	Pilot, 6 (6) Slipstream evaluation from coal, biomass and cement plant flue gases	Range of costs suggested from comparable to COE for MEA process, to 14% lower COE c.f. oxyfuel combustion plant	Technologies developed will be applicable for calcination application and for future air capture	Cement industry is large market with ample experience in handling similar processes	Key technology components (ASU, CPU, CFB) already commercialised to similar scales in other industries CO ₂ -sorbent subject of extensive research	High as end-of-pipe technology. Most applicable to retrofit situations, particularly where additional power generation is required	Ongoing demonstration likely to focus on incorporation into cement plant. Demonstration of energy saving and cost reduction modifications, such as externally heated calciner.	
Oxyfuel combustion processes								
Chemical-looping combustion	2	2	3	2	3	2	1	15
Chalmers University Spanish national research council (CSIC) KIER King Abdullah University of Science and Technology Vienna University of Technology Alstom Nanjing University IFP	Pilot, 5 (2) Slipstream evaluation on a range of combustion flue-gas streams	Approx. 22.5% reduction in COE c.f. 30% MEA	Applications in chemical industries and oxygen production	Sizeable market for fluidised beds systems in oil & gas industry and power sector	Key technology components (ASU, CPU, CFB) already commercialised to similar scales in other industries Oxygen carriers subject of extensive research	Replaces standard combustion plant, therefore not a retrofit technology	Replaces standard combustion plant. Ability of process to produce power not yet demonstrated	

TECHNOLOGY AND TECHNOLOGY DEVELOPERS	LEVEL OF DEMONSTRATION ACHIEVED AND TECHNOLOGY READINESS LEVEL	COST INFORMATION	OTHER APPLICATION OF TECHNOLOGY	SIZE OF EXISTING MARKET	AVAILABILITY AND MATURITY OF TECHNOLOGY COMPONENTS; EASE OF TECHNOLOGY SUPPLY	EASE OF RETROFIT	ENGINEERING FOR CARBON CAPTURE & STORAGE/RESEARCH & DEVELOPMENT REQUIRED	TOTAL SCORE
SINTEF University of Darmstadt Ohio State University								
Oxyfuel gas turbines NET Power Clean Energy Systems University of Graz	2 Pilot, 2–5 (2–5) Evaluated on natural-gas flue-gas streams	1 Approx. 6% reduction in LCOE c.f. NGCC with 30% MEA	3 Existing market for gas turbines	1 Non-existent	2 Most of the components required are commercially available Only the turbine and recuperating heat exchanger are at a lower TRL Adaption of turbines typically being completed in collaboration with industry suppliers	2 Medium. Replacement of traditional combustion systems but closed SC–CO ₂ cycle could replace steam cycle	2 Pilot-scale demonstration of full system required. Now under way for NET Power	13
High-temperature air-separation membranes Air Products Praxair RWTH Aachen Ricerca Sul Sistema Energetico Forschungszentrum Juelich Shandong University of Technology	2 Pilot, 4–7 (4–7)	1 5–12% reduction in LCOE c.f. plant using cryogenic ASU process	3 Existing market for air separation	1 Negligible	3 Membrane materials developed and module concepts defined	1 Low. Replacement of traditional combustion systems	2 Long-term evaluation of membrane systems required to demonstrate stability and durability in process environment	13
Pressurised oxyfuel combustion Unity Power Alliance Washington University in St Louis	2	2 Approx. 22% reduction in LCOE c.f. PCC with 30% MEA	3 Potentially large market i.e. the combustion system market	1 Non-existent	2 ASU and CPU components already commercialised to similar scale in other industries	1 Low. Replacement of traditional combustion systems	1 Ongoing work developing further efficiency aspects, such as pressurised removal of SO _x and NO _x components	12

TECHNOLOGY AND TECHNOLOGY DEVELOPERS	LEVEL OF DEMONSTRATION ACHIEVED AND TECHNOLOGY READINESS LEVEL	COST INFORMATION	OTHER APPLICATION OF TECHNOLOGY	SIZE OF EXISTING MARKET	AVAILABILITY AND MATURITY OF TECHNOLOGY COMPONENTS; EASE OF TECHNOLOGY SUPPLY	EASE OF RETROFIT	ENGINEERING FOR CARBON CAPTURE & STORAGE/RESEARCH & DEVELOPMENT REQUIRED	TOTAL SCORE
GTI	Pilot, 5, with ongoing development work progressing the technologies to TRL 6 Evaluated on coal and natural-gas flue-gas streams				For GTI system, in-bed heat exchangers have been evaluated since 1980s Standard oxyfuel combustion processes have been demonstrated to 30-MW _e scale but not at pressure			
Pre-combustion capture								
H₂ separation membranes Arizona State University SRI International Media and Process Technologies University of Southern California University at Buffalo SINTEF Reinersten AS Los Alamos National Laboratories MTR Eltron Research and Development Worcester Polytechnic Institute	2 Pilot, 5–6 (5) Evaluation on gasifier syngas slipstream	1 Estimate 7–12.5% reduction in COE c.f. IGCC plant using Selexol (10% lower than IGCC with Selexol)	3 Also used in H ₂ production, steam methane reforming processes	3 Polymeric membranes are used for hydrogen recovery in chemical industry; niche application for metallic membranes	3 Mature except for membrane modules Large-scale membrane production applied in other industries (polymeric membranes, reverse osmosis; metallic membranes, steam methane reforming)	3 High as end-of-pipe technology	2 Long-term pilot-scale evaluation integrated with power plant	17
CO₂ separation membranes MTR	2 Pilot, 5–6 (5)	1	3	3	3 Mature except for membrane modules	3 High as end-of-pipe technology	2 Long-term pilot-scale evaluation integrated with power plant	17

TECHNOLOGY AND TECHNOLOGY DEVELOPERS	LEVEL OF DEMONSTRATION ACHIEVED AND TECHNOLOGY READINESS LEVEL	COST INFORMATION	OTHER APPLICATION OF TECHNOLOGY	SIZE OF EXISTING MARKET	AVAILABILITY AND MATURITY OF TECHNOLOGY COMPONENTS; EASE OF TECHNOLOGY SUPPLY	EASE OF RETROFIT	ENGINEERING FOR CARBON CAPTURE & STORAGE/RESEARCH & DEVELOPMENT REQUIRED	TOTAL SCORE
CO2CRC	Evaluation on gasifier syngas slipstream	Estimate 7% reduction in COE c.f. IGCC plant using Selexol	Membranes will continue to be used in natural-gas market, particularly if their performance has been improved	Polymeric membranes are used in natural-gas treatment for CO ₂ -removal	Large-scale membrane production applied in other industries (polymeric membranes, reverse osmosis)			
Solid sorbents	2	1	3	3	3	3	2	17
TDA CO2CRC Air Products	Pilot, 6 Evaluation on gasifier syngas slipstream	Estimate 5–10.5% reduction in COE c.f. IGCC plant using Selexol	Existing market will continue to be served	Solid sorbents used in steam methane reforming for final purification and removal of CO ₂	Technology for solid sorbents is commercially available	High as end-of-pipe technology	Long-term pilot-scale evaluation integrated with power plant	
Chemical liquid absorbents	2	1	3	2	3	3	2	16
CO2CRC SRI International	Pilot, 5 Evaluation on gasifier syngas slipstream	Estimate 7.5% reduction in COE c.f. IGCC plant using Selexol	Natural-gas treatment	Limited application of carbonate solutions for gas treatment	Absorbents should be relatively easy to manufacture. Processes use standard liquid-absorbent plant components	High as end-of-pipe technology	Long-term pilot-scale evaluation integrated with power plant	
Sorbent-enhanced water–gas shift	2	2	2	1	2	3	2	14
KIER Southern Research University of Illinois at Urbana-Champaign Energy research Centre of the Netherlands Politecnico di Milano SINTEF Air Products BP	Pilot, 4–6 (5) Evaluation on gasifier syngas slipstream	Estimate 8–18% reduction in COE c.f. IGCC plant using Selexol (7% reduction in LCOE c.f. IGCC with Selexol)	Sorbents and catalysts developed will be used in other applications	Non-existent	Catalysts and solid sorbents available; integrated reactor concepts require further development	High as end-of-pipe technology	Long-term pilot-scale evaluation integrated with power plant	

TECHNOLOGY AND TECHNOLOGY DEVELOPERS	LEVEL OF DEMONSTRATION ACHIEVED AND TECHNOLOGY READINESS LEVEL	COST INFORMATION	OTHER APPLICATION OF TECHNOLOGY	SIZE OF EXISTING MARKET	AVAILABILITY AND MATURITY OF TECHNOLOGY COMPONENTS; EASE OF TECHNOLOGY SUPPLY	EASE OF RETROFIT	ENGINEERING FOR CARBON CAPTURE & STORAGE/RESEARCH & DEVELOPMENT REQUIRED	TOTAL SCORE
Clathrates Los Alamos National laboratories	1 Bench-scale, 4 Evaluation on synthetic syngas stream	1 Comparable COE to IGCC process with Selexol	3 Gas- separation market	1 Non-existent	1 Potential to use conventional equipment; however, demonstration showing suitable heat transfer and plugging avoidance required	3 High as end-of-pipe technology	1 Pilot-scale evaluation treating process gas stream required	11

All of the 23 technologies listed in Table 38 are worthy of further evaluation. As it was not possible to analyse all of these within this project, we selected the following five representative technologies (four post-combustion and one oxyfuel) for further analysis in a techno-economic assessment. This selection was based not only on the technology ranking, but also the technology’s current level of development, and wider interest as evidenced by plans for ongoing larger scale demonstration or further research funding. The selected technologies have all received, and continue to receive, funding and investment from government and private investors.

1. MTR Polaris membrane-based process
2. Calcium-looping
3. IFPEN DMX liquid–liquid separating process
4. Inventys VeloxoTherm solid sorbent
5. Net Power Allam cycle

Amine-based PCC is evaluated in detail in Part II of this report. Therefore, additional liquid-absorbent technologies were not considered here for further evaluation.

6.3 Evaluation of potential for emerging technologies to further reduce cost

The techno-economics of the shortlisted coal and gas-fired CO₂ capture technologies were evaluated by comparing the LCOE cost range with that of the new benchmark PCC technology, PZ/AMP (see Part II of this report), and under a base case and two sensitivity cases.

The gas-fired technologies evaluated are:

- the Allam cycle
- Ca-looping
- membranes
- MEA.

The coal-fired technologies evaluated are:

- Ca-looping
- membranes
- DMX
- VeloxoTherm
- MEA.

These evaluations are based on literature data in the public domain for an nth of a kind plant. MEA has been included because it is the previous benchmark technology. For this assessment we have not completed a bottom up design for each technology based at the same power plant. This would be the best comparison for the cost of the different technologies, but was outside the scope of this report. Instead, we have taken information from cost studies available in the literature. This means that there will be different assumptions between the studies that will affect the final cost data. This will affect the capital and operating cost information used to LCOE. We have tried to minimise the effect of this by adjusting the literature cost information to be consistent with a plant located in the Netherlands, averaging over a range of different studies where possible, and scaling the technologies to the same unit size. The different assumptions used in the cost studies means that the cost data for the different technologies should not be compared directly. Rather, the aim here is to provide the range of cost predictions for the new and emerging CO₂ capture technologies, and provide an indication of their potential to lower the cost of CO₂ capture from power plant.

As we have used information from different literature studies, we have also not explored the energy efficiency of the different technologies in detail. Information on this can be approximated however by the efficiency penalty applied to the power station from the addition of the CCS plant. Thus processes that achieve higher power station efficiencies tend to have the higher overall energy efficiency (see Appendix A).

6.3.1 Method

Levelised cost of electricity (LCOE)

LCOE is a simple metric that is commonly used for comparing electricity generation technologies. It includes all costs of generation, but no financial factors such as revenue, depreciation or taxation.

It can include greenhouse gas emission-reduction incentives and, in the case of CCS, the cost of CO₂ transport and storage. The formula for LCOE is:

$$LCOE = \frac{CRF \times Capital}{8760 \times Capfac} + \frac{O\&M_{fixed}}{8760 \times Capfac} + O\&M_{var} + \frac{3600 \times F}{Eff} + GHG_{store} \times T\&S$$

where *CRF* is the capital recovery factor, *Capital* is the capital cost in €/kW, 8760 are the number of hours in a year, *Capfac* is the capacity factor (as a fraction), *O&M_{fixed}* is the fixed operations and maintenance (O&M) cost in €/kW, *O&M_{var}* is the variable O&M cost in €/kWh, *F* is the cost of fuel in €/GJ (LHV), *Eff* is the plant efficiency (as a fraction in LHV), *GHG_{store}* are the CO₂ emissions to be stored in tCO₂-e/kWh, and *T&S* is the CO₂ transport and storage cost in €/tCO₂-e stored.

Capital recovery factor (CRF)

The *CRF* converts the capital cost to an annual amortised payment and is given by:

$$CRF = CFM \frac{d \times (1 + d)^L}{(1 + d)^L - 1}$$

where *d* is the discount rate (as a fraction) and *L* is the plant lifetime in years.

Construction finance multiplier (CFM)

Interest during construction has also been included, as a construction finance multiplier (*CFM*). It has been assumed that all plants have a three-year construction period and the payments over this period are made as follows: Year 1 = 20%, Year 2 = 45% and Year 3 = 35%. The *CFM* is given by:

$$CFM = 20\% \times (1 + d)^3 + 45\% \times (1 + d)^2 + 35\% \times (1 + d)$$

All costs are presented in EUR (€) 2015. Annual average exchange rates were used to convert costs from USD to EUR¹ and an inflation calculator² was used to convert costs from earlier years to the year 2015.

6.3.2 LCOE parameter estimates

The parameters with the greatest influence on LCOE are capacity factor and capital cost (CSIRO, 2011). Fuel cost can be important for gas-fired power stations, and discount rate has a secondary impact. To avoid these issues, in this study the same capacity factor (85%) has been used for all technologies and cases. The gas price, coal price and discount rate are the same for all technologies, as shown in Table 39.

¹ <https://www.ofx.com/en-au/forex-news/historical-exchange-rates/yearly-average-rates/>

² <https://www.inflationtool.com/euro?amount=1&year1=2011&year2=2015>

Table 39 Levelised cost of electricity parameters used in this study

CRITERIA	BASE CASE	SENSITIVITY 1	SENSITIVITY 2
Coal price, €/GJ (LHV)	2.5	1	4
Natural-gas price, €/GJ (LHV)	6	3	12
Discount rate, %	8	5	10
Plant life, years	25	40	25
CO ₂ transport and storage cost, €/tCO ₂ stored	10	0	20

The capital cost is the key factor that can vary between studies, even when analysing the same technology. All capital costs were converted to be consistent with a plant location in the Netherlands. This meant adjusting the US costs by factors for materials, labour costs and labour productivity³. The factors were sourced from Table 5 in IEAGHG (2018b). In studies that did not provide a breakdown of the costs by materials and labour, an average of the factors was used to adjust the costs.

The capital cost is also influenced by the scale of the plant. Therefore, a scaling factor of 0.6 has been included to adjust the capital costs so all plants can be examined at the same unit size (unit size of PZ/AMP plant, i.e. 761.3 MW_{net} for gas-fired and 684.4 MW_{net} for coal-fired technologies). After making that adjustment, the capital costs were averaged over all studies for the same technology. Some technologies, i.e. gas-fired membranes, gas-fired Ca-looping, VeloxoTherm and DMX, had only one source of costs; therefore, we were unable to use an average value. All other parameters that are used to calculate the LCOE were also averaged over all available studies, or the single-source value was used. Several unit sizes were examined, including the average unit size per technology, the minimum and maximum of all technologies, the PZ/AMP unit size and the reference case (non-CCS) unit size. Appendix A contains all of the averaged parameters used.

6.3.3 Emissions costs

The CO₂-capture cost and the CO₂-avoidance cost were calculated for all CCS technologies and cases at the unit scale of PZ/AMP (761.3 MW_{net} for gas-fired and 684.4 MW_{net} for coal-fired technologies). The formula for CO₂-capture cost in €/tCO₂ is given by:

$$CO_2 \text{ capture cost} = \frac{LCOE_{capture} - LCOE_{ref}}{CO_2 \text{ captured}}$$

where $LCOE_{capture}$ is the LCOE of the capture technology in €/MWh, $LCOE_{ref}$ is the LCOE of the technology without capture in €/MW, and $CO_2 \text{ captured}$ is the amount of CO₂ captured by the CCS technology, in tonnes.

³ The location factors are all 1 for the Netherlands and 0.94 for materials, 0.95 for labour costs and 0.92 for labour productivity in the US.

The formula for CO₂-avoidance cost in €/tCO₂ is given by:

CO₂ avoidance cost

$$= \frac{LCOE_{capture} - LCOE_{ref}}{\left(\frac{CO_2emissions}{Electricity\ generation}\right)_{ref} - \left(\frac{CO_2emissions}{Electricity\ generation}\right)_{capture}}$$

where *ref* refers to the technology without capture and *capture* refers to the technology with CCS.

6.3.4 Potential for future cost reductions

CSIRO's Global and Local Learning Model – Electricity (GALLM-E) is used to project the future cost of electricity-generation technologies in Australia (Graham et al. 2018, Hayward and Graham 2017, Hayward and Graham 2013). GALLM-E includes 24 generic electricity generation and energy storage technologies, including coal and gas with CCS. It also features:

- 13 world regions
- technology learning at the global and regional level
- regional climate policies and carbon pricing
- regional electricity demand, installed capacities of existing generation and local fuel prices and costs.

GALLM-E can also be linked with a transport model and an energy storage model to provide greater granularity in terms of battery, electric vehicle, fuel-cell and fuel-cell electric vehicle uptake. More information on GALLM-E methods can be found in the studies listed above.

There are four different CCS technologies in GALLM-E – black coal, brown coal, gas and biomass. Each of these technologies is further divided into three components, which have different learning rates:

- CCS build – has learning at the regional/local level, as it represents the costs of labour for construction of CCS plants
- CCS equipment – has learning at the global level, as it represents the purchased equipment of CCS plants
- CCS balance of plant – represents the mature remainder of the rest of the plant and has no learning.

There is shared learning of CCS build and CCS equipment across all of the CCS technologies. This means that when, for example, a coal with CCS plant is constructed in the model, the cost reduces due to learning by doing for all CCS technologies.

In this study, the generic black coal and gas CCS-technology parameters in GALLM-E were replaced with the parameters for PZ/AMP, and the model has been re-run to allow comparison of the new baseline CCS technology, PZ/AMP, with the other technologies in GALLM-E.

6.4 Results

The LCOE and emission summaries are presented separately below for gas-fired and coal-fired technologies. Further information on the literature sources and values used in the cost assessments and calculations of LCOE can be found in Appendix A.

6.4.1 Gas-fired technologies

The LCOE range for the different technologies and the impact of the sensitivity cases is shown in Figure 16, where the LCOE of all technologies is calculated at the PZ/AMP unit size, i.e. 761 MW_{net}.

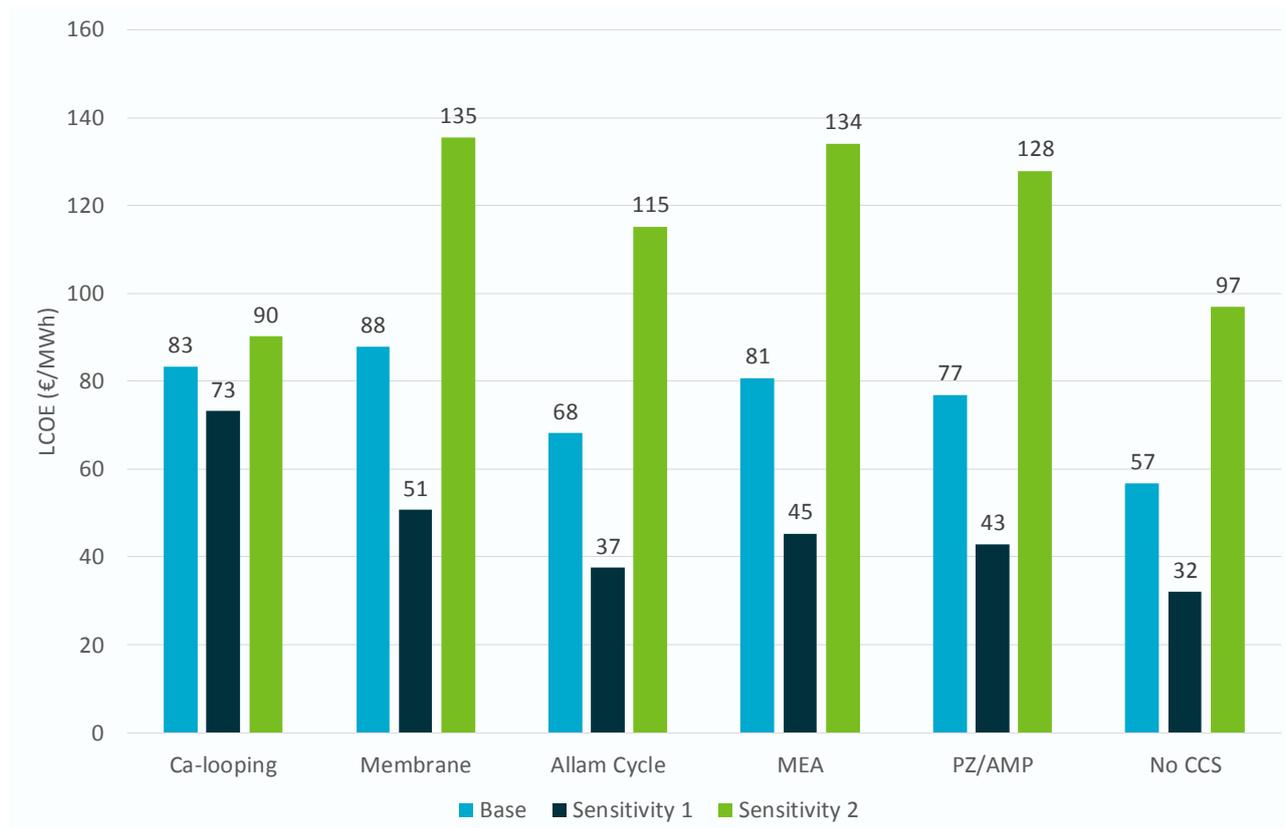


Figure 16 Comparison of levelised cost of electricity (LCOE) of gas-fired technologies

CCS = carbon capture and storage; MEA = monoethanolamine; PZ/AMP = piperazine/amino-methyl-propanol

* Note: gas price included in variable O&M cost for Ca-looping case. This meant that it was not possible to separate out the gas price for the sensitivity analysis, and is why there is limited variation in cost between the sensitivity cases for this technology.

The range in base costs of the CCS technologies is from 68–88 €/MWh, with the Allam cycle being the least cost and membrane the most expensive. In addition, the Allam cycle captures more than 98% of emissions, whereas the other technologies only capture 90%. A comparison of the emissions captured and stored, and emissions released is shown in Figure 18. Membrane has a lower efficiency, which can be seen in the relative difference in emissions captured between membranes and the other technologies.

Under Sensitivity 1, the range in costs is from 37–73 €/MWh, with the Allam cycle being the least cost and Ca-looping the most expensive, as in the base case. However, while the LCOE of the Allam cycle has reduced by 45%, the LCOE of Ca-looping has only reduced by 12% compared with the base case. Under Sensitivity 2, the range in costs is from 90–135 €/MWh, with Ca-looping now the least

expensive and membrane the most expensive. The reason why Ca-looping has so little variation is that the gas price was included in the variable O&M cost and was not possible to separate out, thus the sensitivity cases are not affected by changes to the gas price. Therefore, ignoring Ca-looping's sensitivity cases, under all sensitivity cases Allam cycle is the least expensive and membrane is the most expensive. Under Sensitivity 2, the Allam cycle and membrane LCOEs have increased by 169% and 153% over the base case, respectively.

A breakdown of the base case LCOE into its cost components for each technology is shown in Figure 17. It can be seen from the figure that fuel cost makes up the largest proportion of the LCOE of each technology, followed by Capex, O&M and finally CO₂ transport and storage. Gas-fired electricity generation technologies typically have a larger fuel component to their LCOE compared to coal-fired technologies because of the higher cost of gas compared to coal.

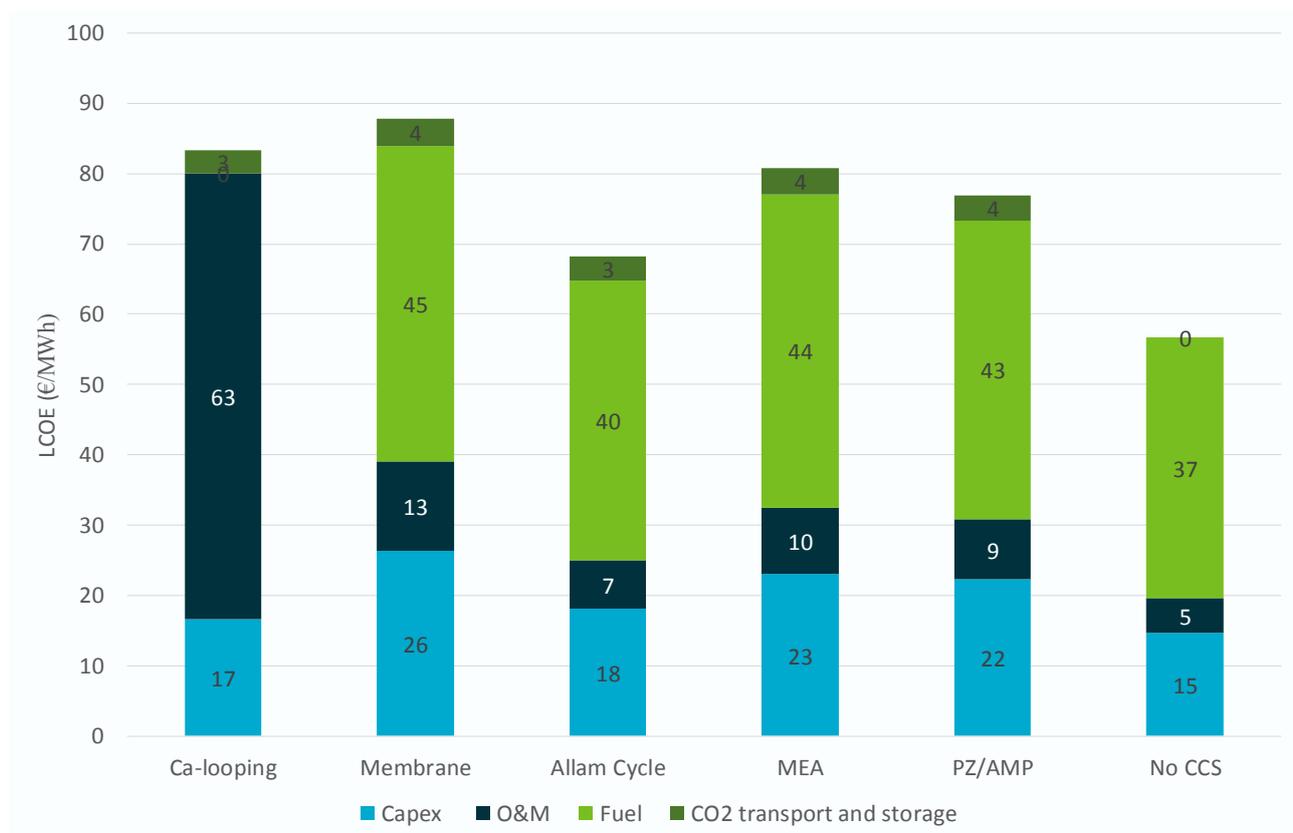


Figure 17 Breakdown of the base case LCOEs of gas-fired technologies into components. Note that the O&M cost in Ca looping also contains the fuel cost

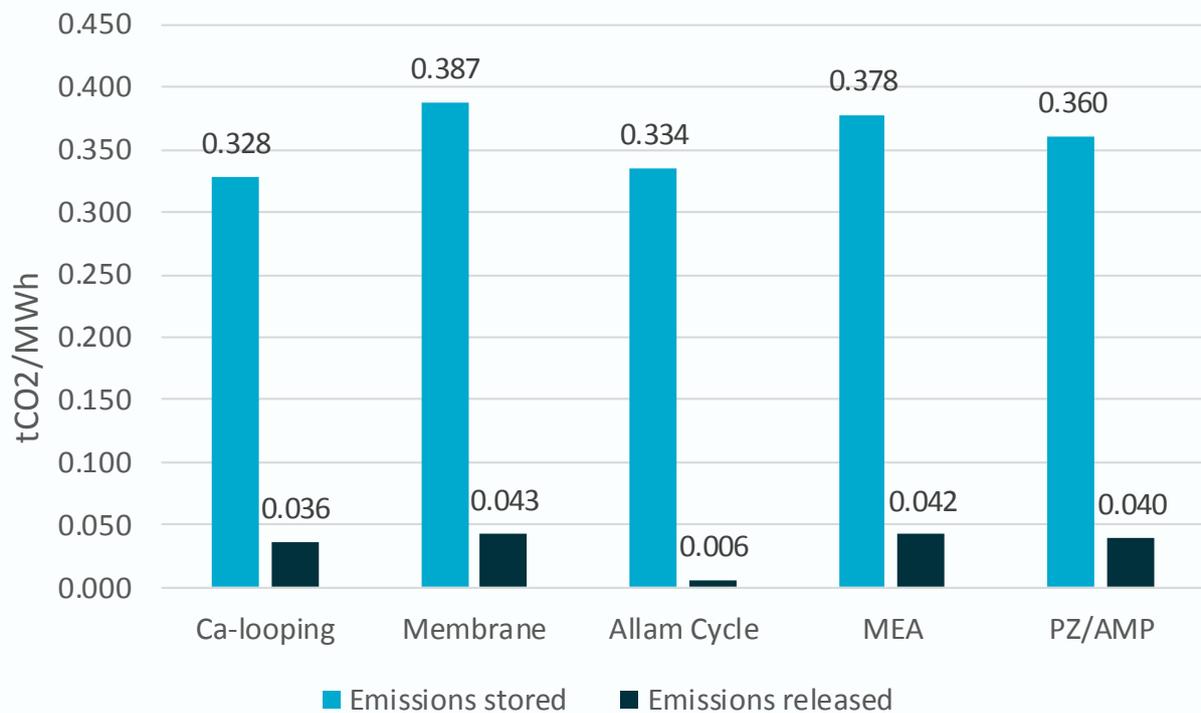


Figure 18 Comparison of CO₂ emissions from gas-fired technologies with carbon capture and storage only

MEA = monoethanolamine; PZ/AMP = piperazine/amino-methyl-propanol

The impact of unit scale on the LCOE is shown in Figure 19, where the base-case LCOE has been calculated at the minimum (604 MW), middle (761.3 MW) and largest (882 MW) scales of all technologies. The largest variation occurs in the LCOE of Ca-looping, where the range is 79–91 €/MWh. This is because the fixed and variable O&M costs are based on a percentage of capital cost; thus, a change in unit size not only affects the capital, but also the O&M costs. The smallest variation among the CCS technologies occurs in the LCOE of the Allam cycle, where the range is 68–71 €/MWh. Unit size has limited impact on the LCOE of this technology.

A comparison of each technology at its average unit size with the matching no-CCS (reference) technology for the base case is shown in Figure 20. The largest variation occurs for membrane, where the no-CCS technology is 37% lower in cost than the CCS technology. The smallest variation (16%) occurs for the Allam cycle.

The CO₂-avoidance cost is shown Figure 21 under the base and both sensitivity cases. Ca-looping only has results under the base case, because given that the gas price could not be varied, it was not possible to produce a credible avoidance cost under the sensitivity cases. The avoidance cost ranges from 33–100 €/MWh under the base scenario, where again the Allam cycle is the lowest and membrane is the highest. This cost could be compared with a carbon price, and if the avoidance cost is lower, it is less costly to use CCS than to purchase permits.

The CO₂-capture cost is shown in Figure 22 under all scenarios. The trends are the same as those of the CO₂-avoidance cost under the base scenario, but the values are lower.

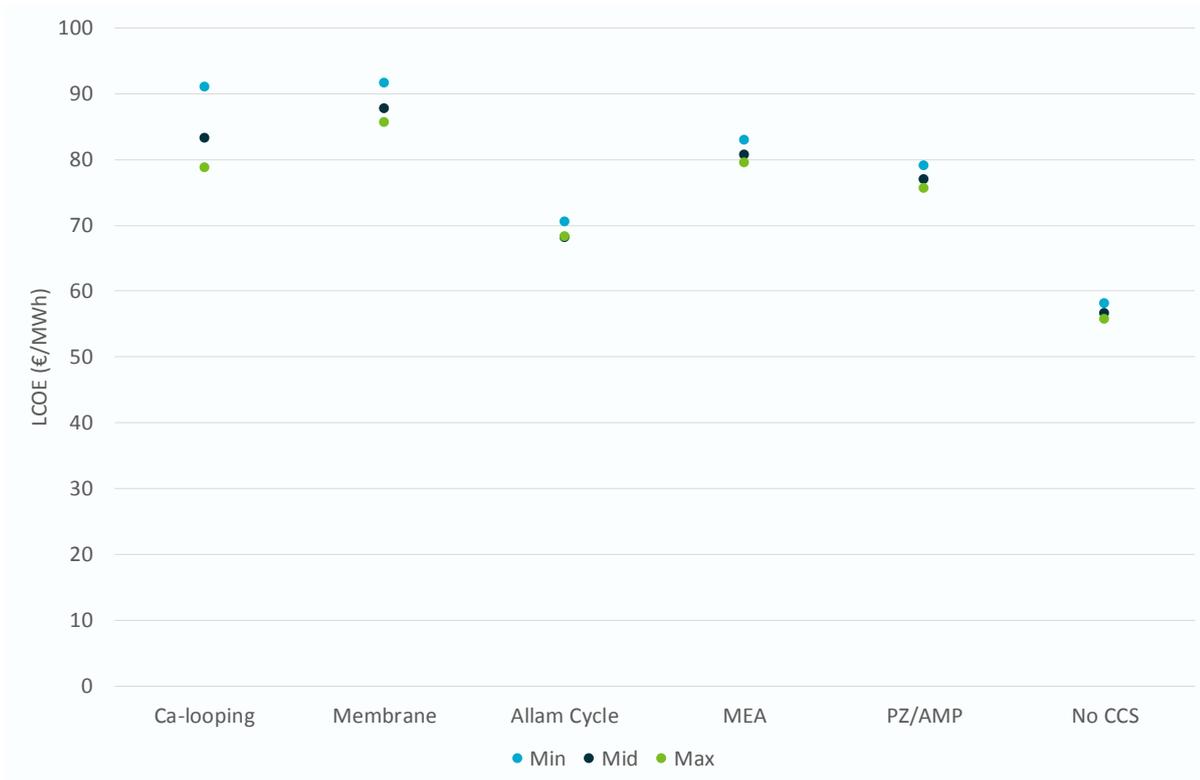


Figure 19 Comparison of levelised cost of electricity (LCOE) of gas-fired technologies at different unit sizes
 CCS = carbon capture and storage; MEA = monoethanolamine; PZ/AMP = piperazine/amino-methyl-propanol

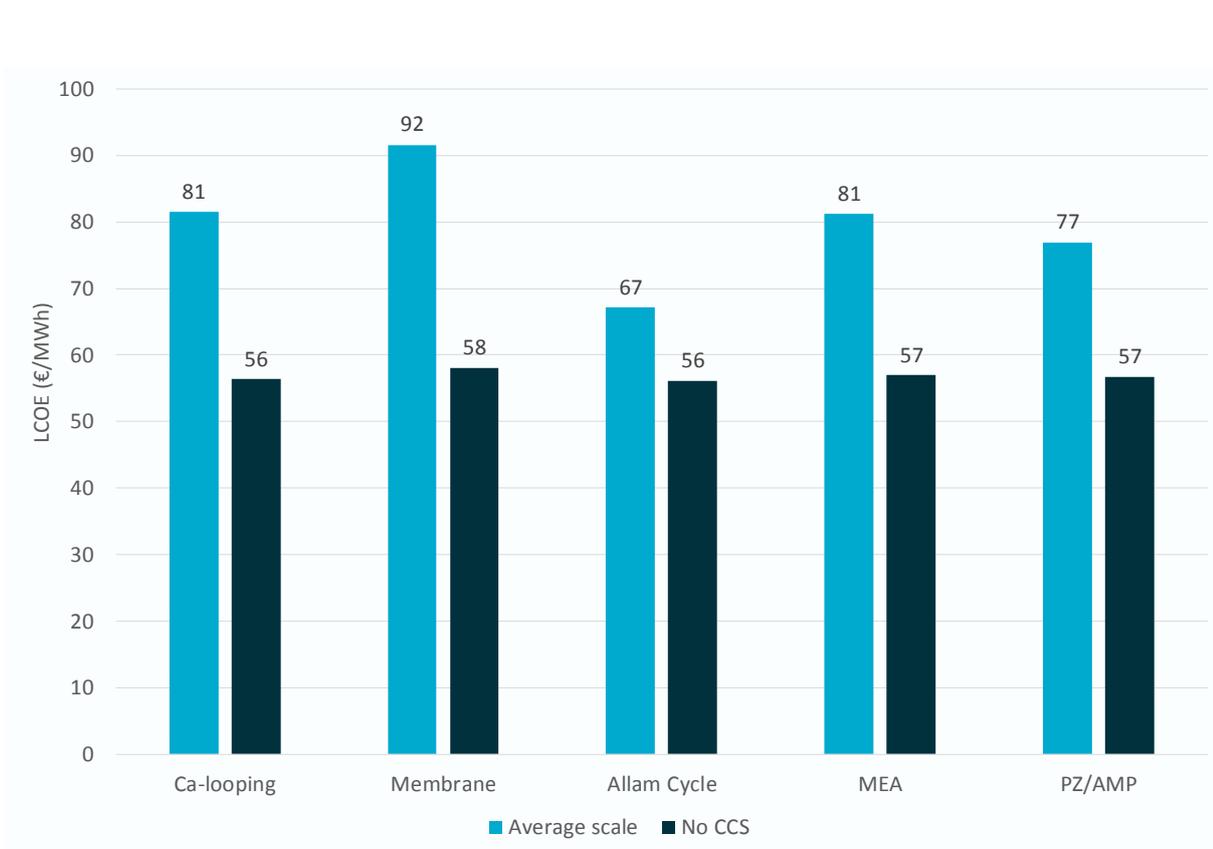


Figure 20 Comparison of levelised cost of electricity (LCOE) of gas-fired technologies with and without carbon capture and storage (CCS)

MEA = monoethanolamine; PZ/AMP = piperazine/amino-methyl-propanol

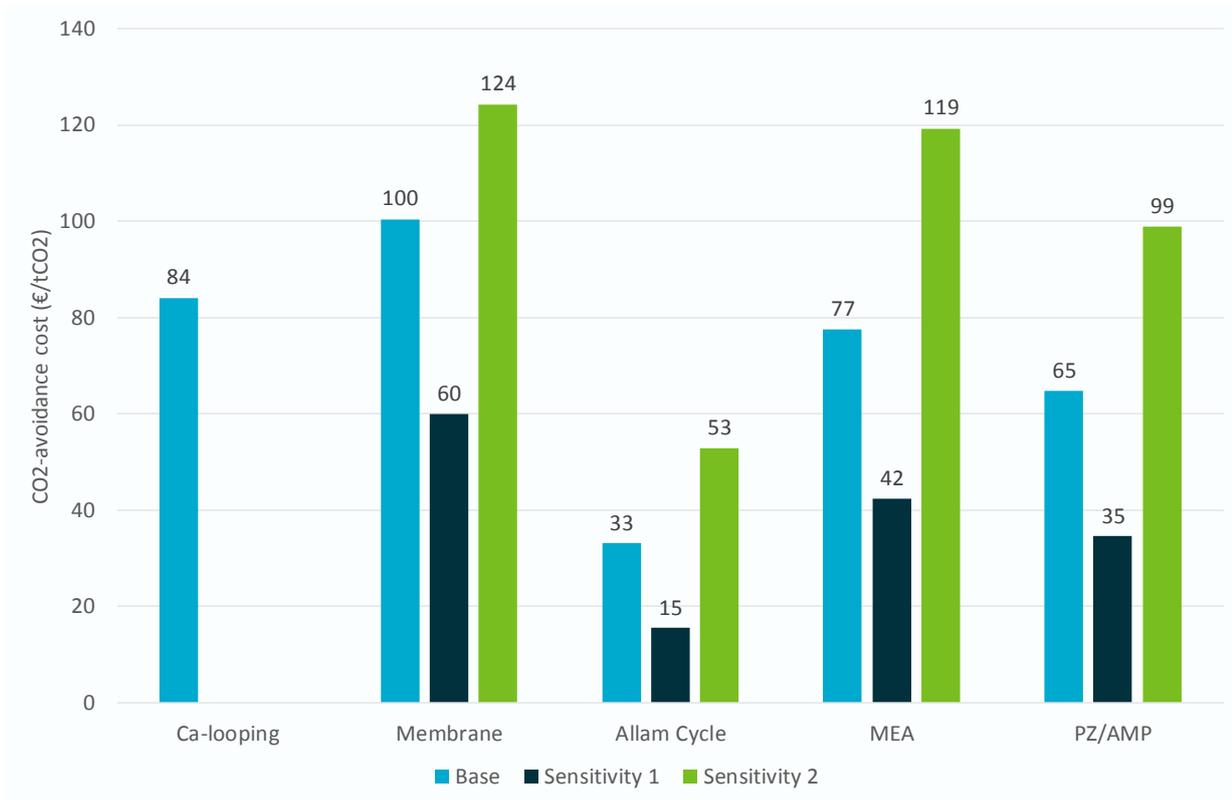


Figure 21 CO₂-avoidance cost for gas-fired carbon capture and storage technologies

MEA = monoethanolamine; PZ/AMP = piperazine/amino-methyl-propanol

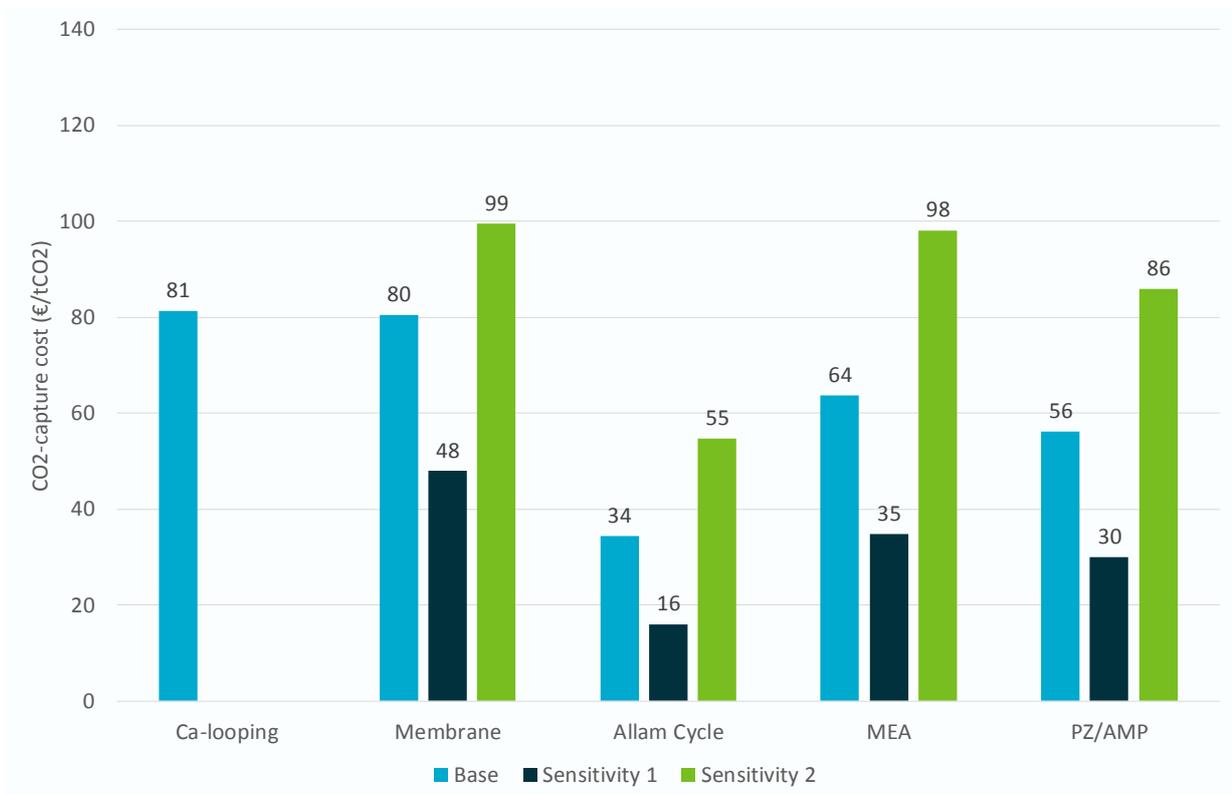


Figure 22 CO₂-capture cost for gas-fired carbon capture and storage technologies

MEA = monoethanolamine; PZ/AMP = piperazine/amino-methyl-propanol

6.4.2 Coal-fired technologies

The LCOE range for the different technologies and the impact of the sensitivity cases, calculated at the scale of PZ/AMP (684 MW_{net}), is shown in Figure 23.

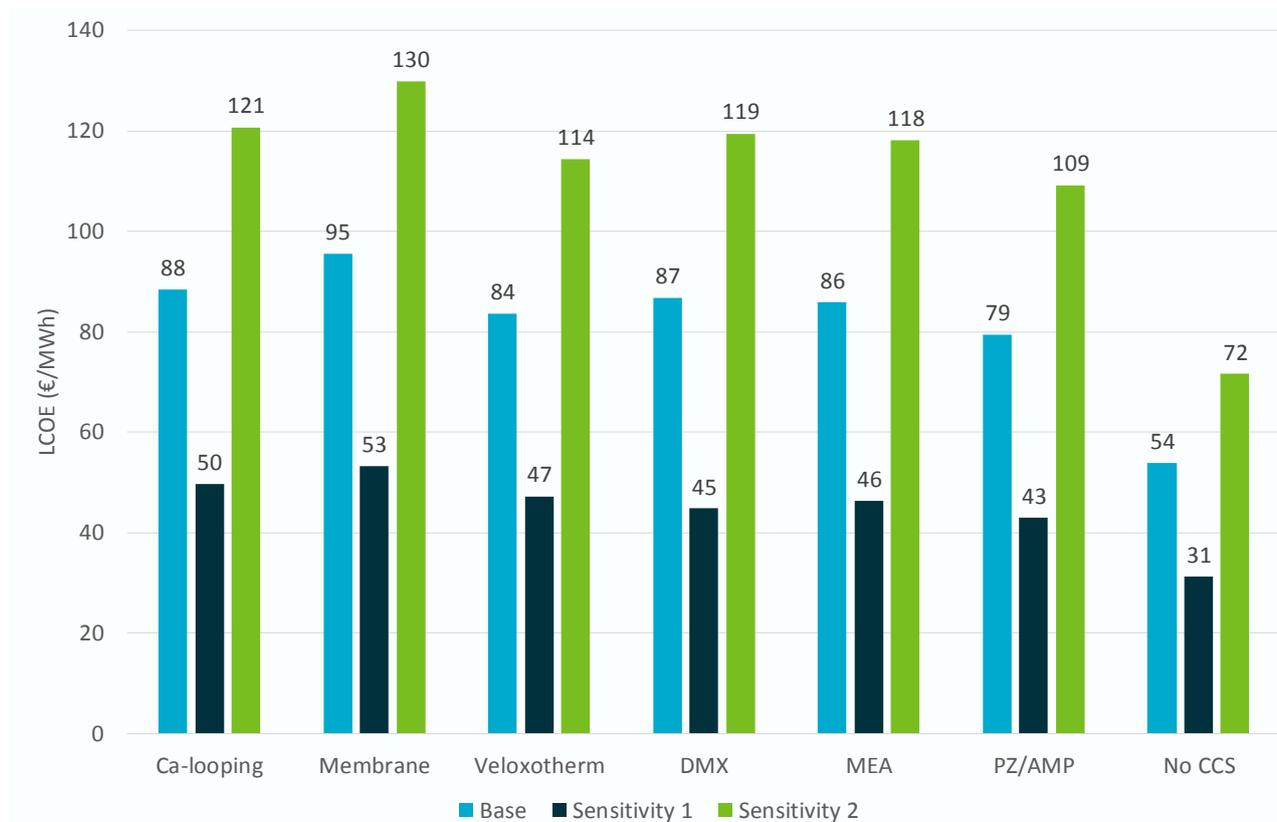


Figure 23 Comparison of levelised cost of electricity (LCOE) of coal-fired technologies

CCS = carbon capture and storage; DMX = proprietary process developed at French Petroleum Institute Energies Nouvelles; MEA = monoethanolamine; PZ/AMP = piperazine/amino-methyl-propanol

The figure shows that there is little variation in the base-case LCOE among the different CCS technologies. The range is 79–95 €/MWh, with PZ/AMP the lowest and membrane the highest in cost. The variation in cost is ~30%. There is even less variation among all technologies in Sensitivity 1, where the range of costs is 43 – 53 €/MWh, where PZ/AMP is again the lowest and membrane is the highest in cost. The variation is only ~20%. Sensitivity 2 has the highest overall costs, from 109–130 €/MWh, with the same technology trends as previously. The percentage range of variation is ~35%. For PZ/AMP and membrane, the difference between the base case and Sensitivity 1 is 46% and 44%, respectively, and between the base and Sensitivity 2 it is 127% and 128%, respectively.

A breakdown of the LCOE of each technology under the base case is shown in Figure 24. In all technologies the largest contribution to the LCOE is from capex, followed by fuel, O&M and lastly CO₂ transport and storage.



Figure 24 Breakdown of the base case LCOEs of coal-fired technologies into components

The emissions stored and emitted from each CCS technology are shown in Figure 25. There is a small amount of variation in emissions, where DMX has the lowest stored and released emissions and membrane the highest. The difference is due to the difference in efficiency of the technologies, which is 36% (LHV) for DMX and 32% (LHV) for membrane.

The impact of unit size/scale on the LCOE is shown in Figure 26 for all technologies under the base scenario. The minimum (550 MW), mid (684 MW) and maximum (886 MW) scales are based on the scales of the smallest (membrane), mid (PZ/AMP) and largest (Ca-looping) average technology scales found in the literature. The impact of scale is fairly uniform across all technologies, with a variation in LCOE of 6–10 €/MWh or ~10%.

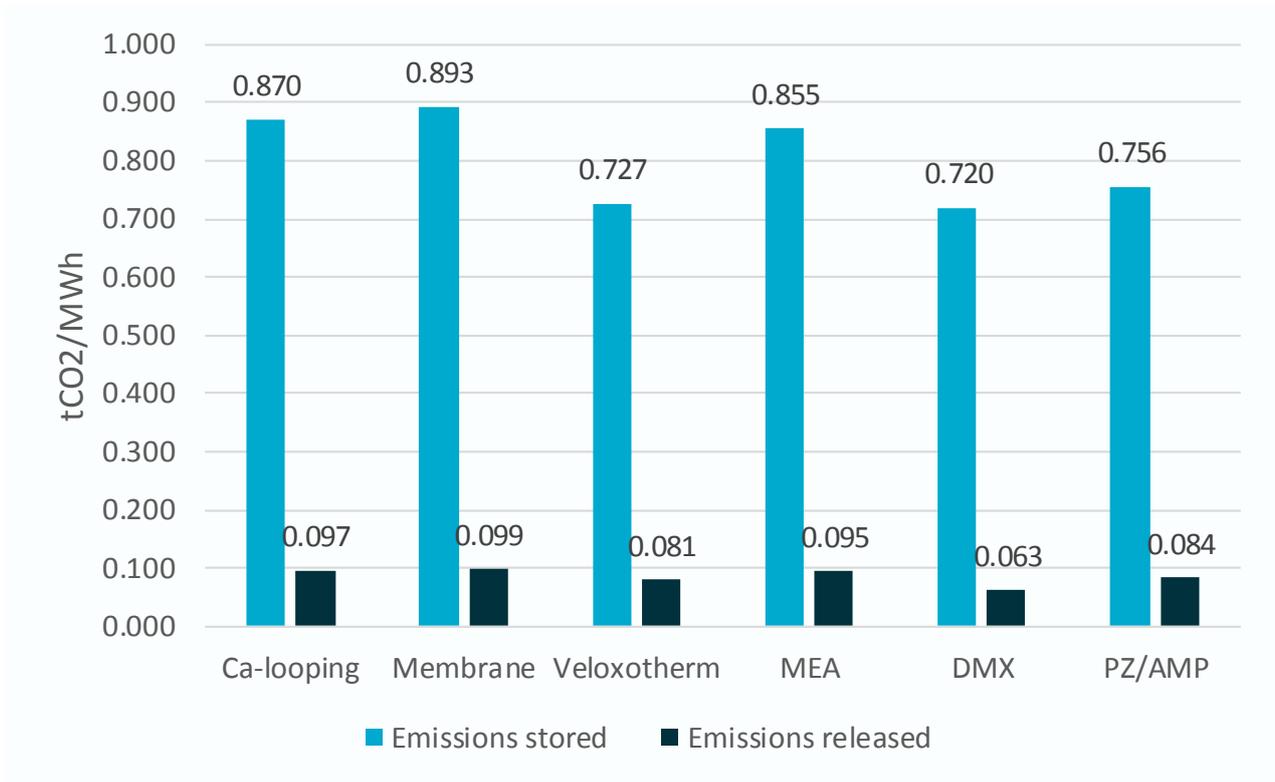


Figure 25 Comparison of CO₂ emissions from coal-fired technologies with carbon capture and storage only

DMX = proprietary process developed at French Petroleum Institute Energies Nouvelles; MEA = monoethanolamine; PZ/AMP = piperazine/amino-methyl-propanol

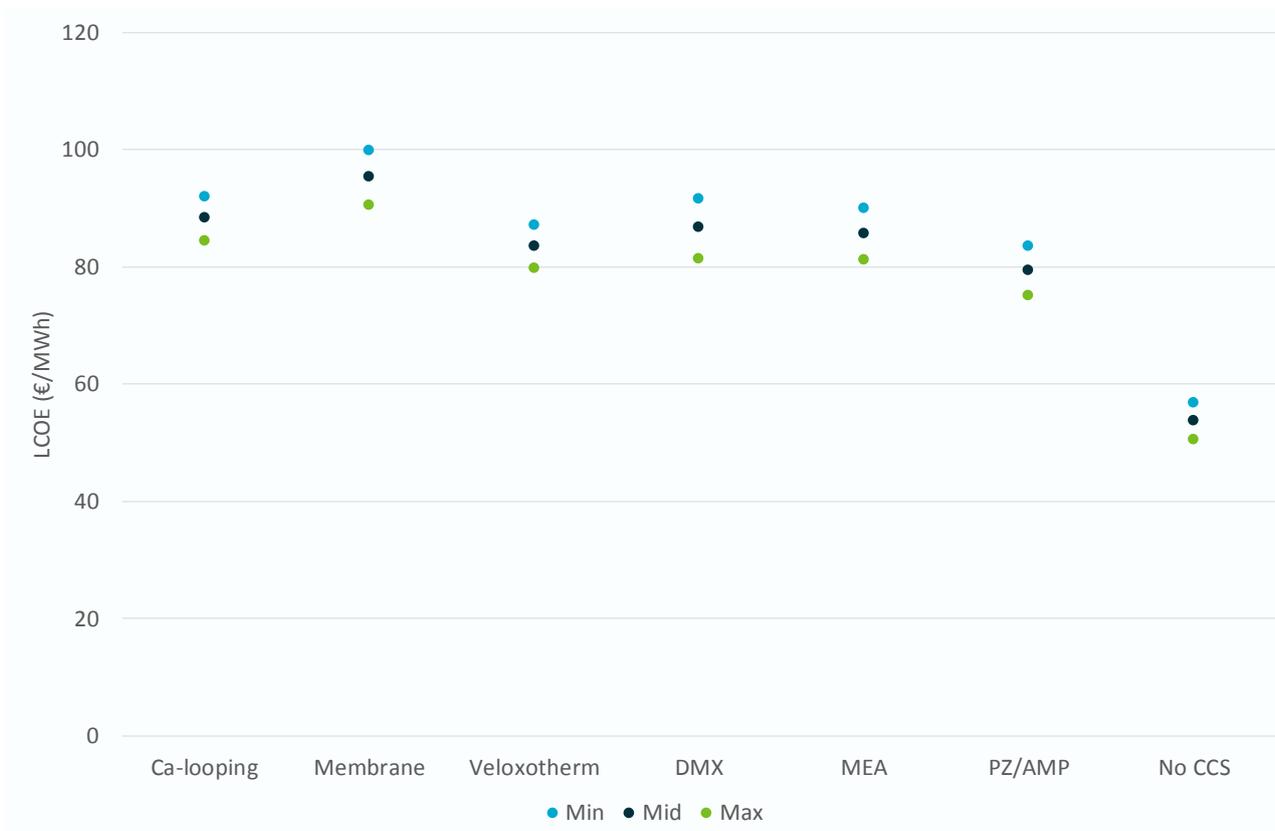


Figure 26 Comparison of levelised cost of electricity (LCOE) of coal-fired technologies at different unit sizes

CCS = carbon capture and storage; DMX = proprietary process developed at French Petroleum Institute Energies Nouvelles; MEA = monoethanolamine; PZ/AMP = piperazine/amino-methyl-propanol

The difference in the base scenario LCOEs with and without CCS at the average scale of each technology is shown in Figure 27. The differences range from 26–43 €/MWh, where the lowest occurs for PZ/AMP and the highest for membrane. PZ/AMP is the lowest-cost coal-fired CCS technology at its average scale in this study; thus, the difference between with and without CCS technologies is lower than membranes, which have the smallest scale (550 MW) and the highest-cost technology.

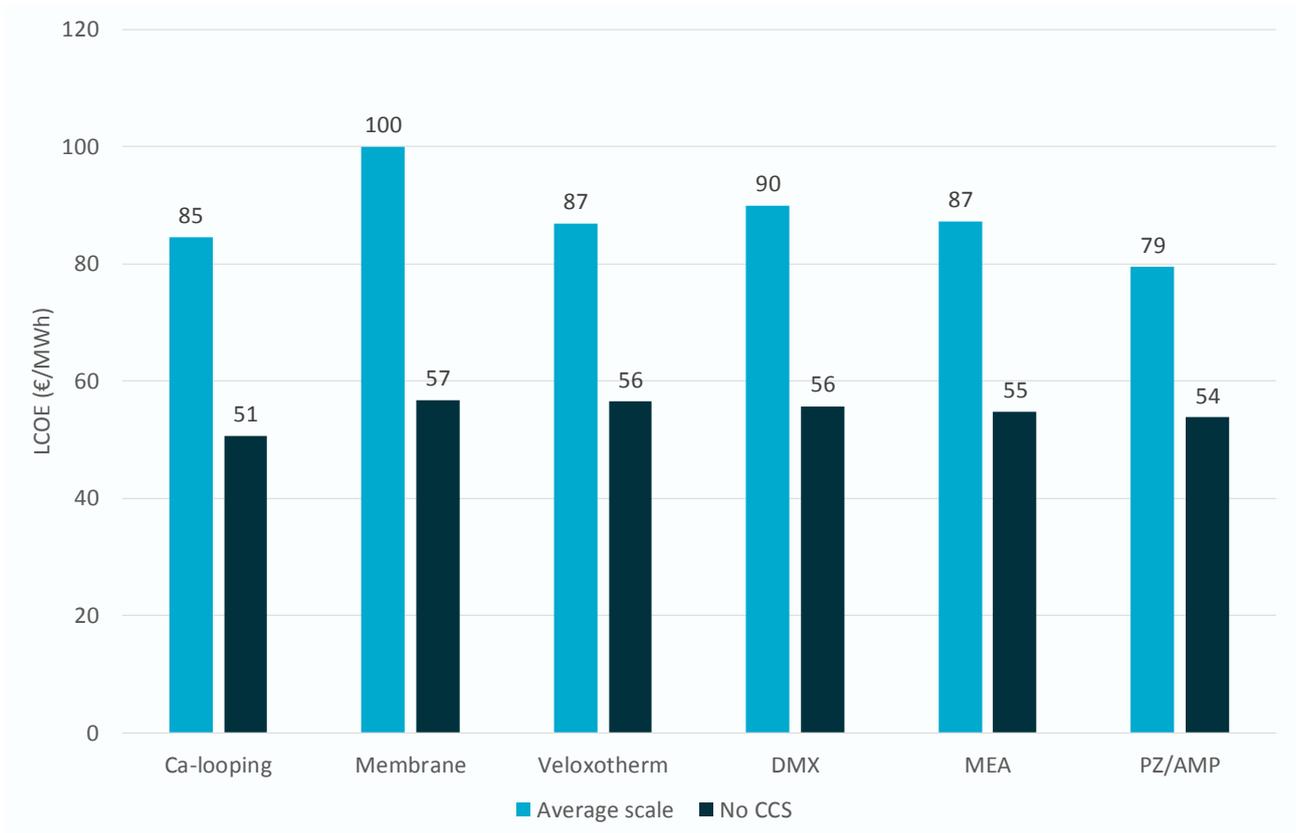


Figure 27 Comparison of levelised cost of electricity (LCOE) of coal-fired technologies with and without carbon capture and storage

CCS = carbon capture and storage; DMX = proprietary process developed at French Petroleum Institute Energies Nouvelles; MEA = monoethanolamine; PZ/AMP = piperazine/amino-methyl-propanol

The CO₂-avoidance cost for all CCS technologies and all scenarios is shown in Figure 28. The lowest-cost and highest-cost technologies are the same across all scenarios. Under the base scenario, the CO₂-avoided costs are in the range 39 - 65 €/tCO₂.

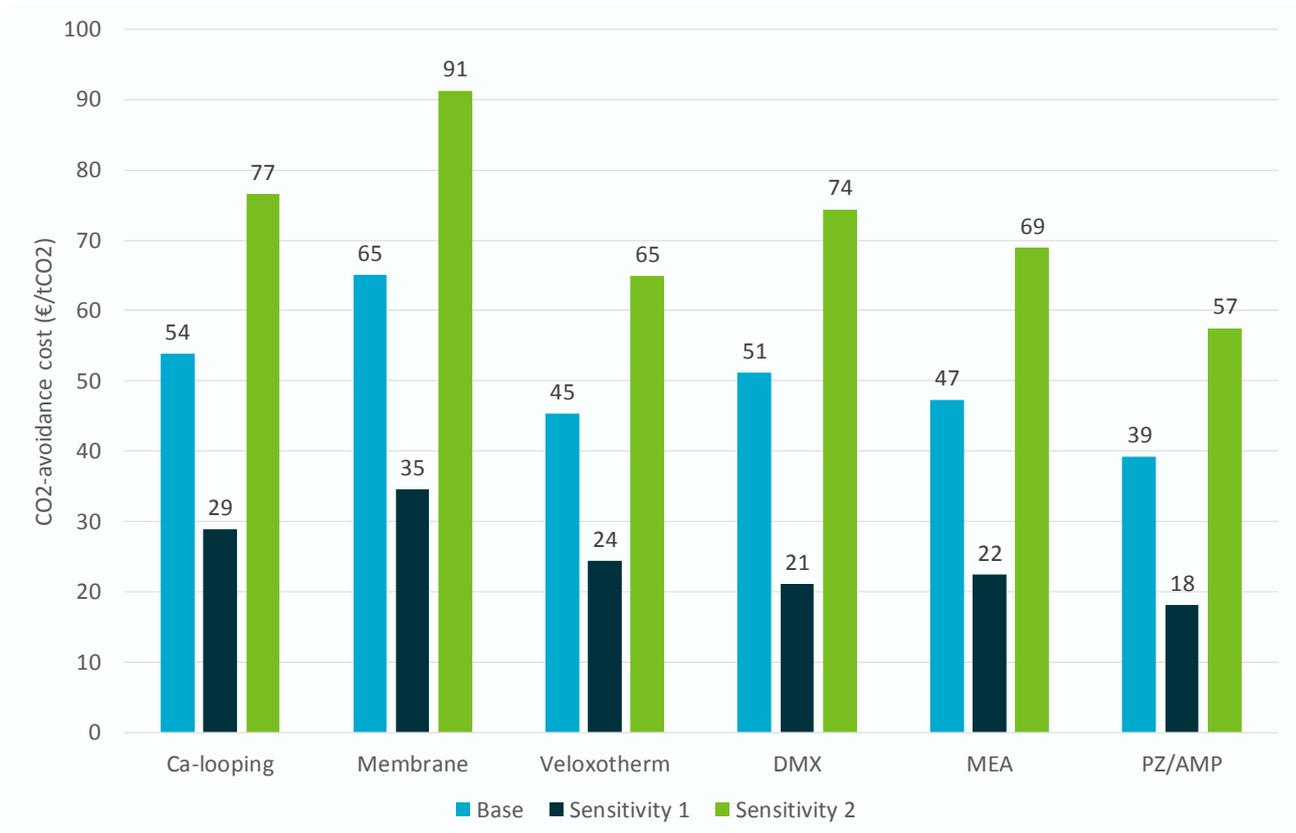


Figure 28 CO₂-avoidance cost for coal-fired carbon capture and storage technologies

DMX = proprietary process developed at French Petroleum Institute Energies Nouvelles; MEA = monoethanolamine; PZ/AMP = piperazine/amino-methyl-propanol

The CO₂-capture cost for all CCS technologies and all scenarios is shown in Figure 29. The trends are similar to those for the CO₂-avoidance cost, except that the values are lower. Under the base scenario the cost ranges from 34–47 €/tCO₂, where PZ/AMP is the lowest and membrane the highest-cost technology, respectively.

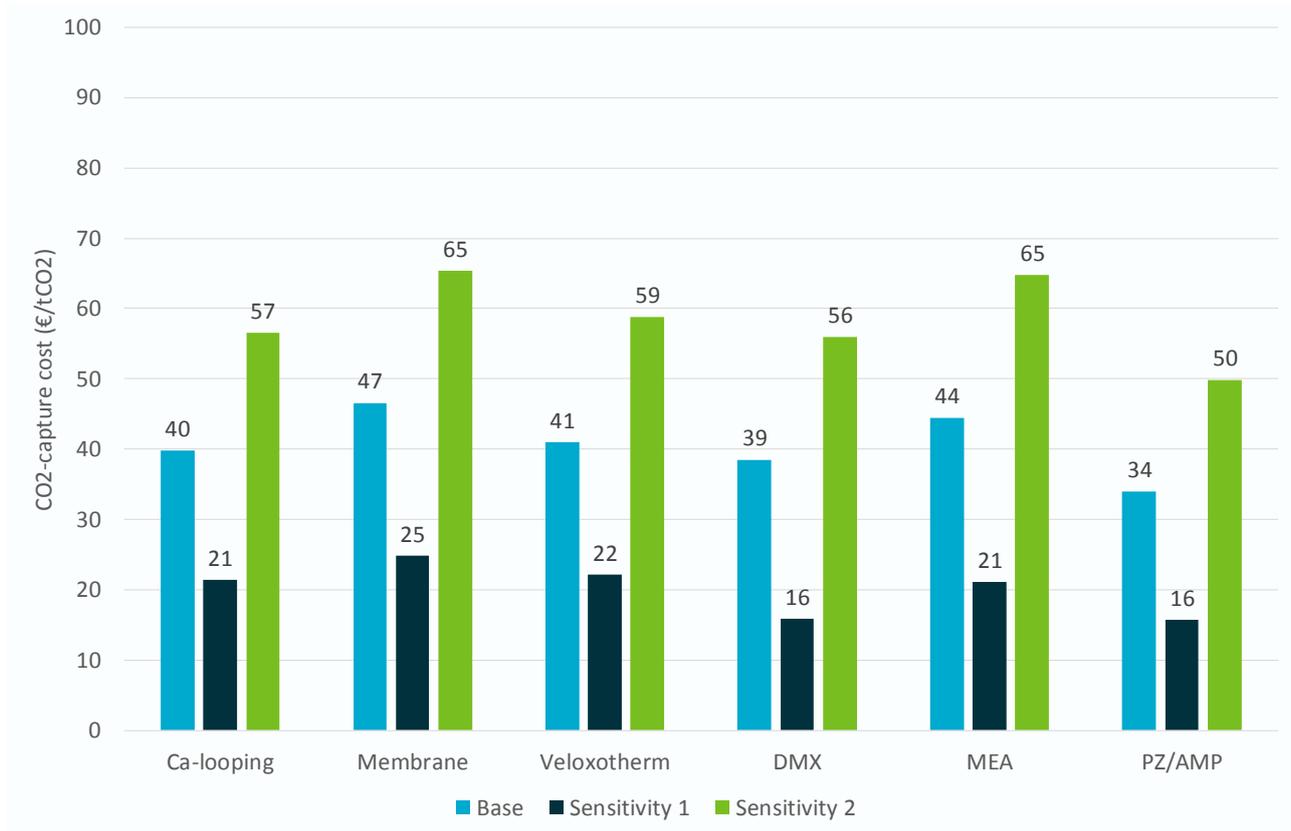


Figure 29 CO₂-capture cost for coal-fired carbon capture and storage technologies

DMX = proprietary process developed at French Petroleum Institute Energies Nouvelles; MEA = monoethanolamine; PZ/AMP = piperazine/amino-methyl-propanol

6.4.3 Potential for future cost reduction and impact on LCOE

Given that the current capital costs of PZ/AMP with CCS are lower than the default CCS technologies in GALLM-E, there was greater uptake of both coal and gas CCS in the model results. The projected global electricity generation from all technologies to the year 2060 is shown in Figure 30 under a 2-degree global-warming carbon-price scenario. The results show that there is a slightly increasing amount of electricity generation from coal PZ/AMP with CCS from 2023 until 2040, when it increases at a higher rate. By 2060, it is contributing 5% to global electricity generation. Gas PZ/AMP with CCS starts later, but reaches a higher level of generation sooner – between 2035 and 2040 – and by 2060, is contributing 7% to global electricity generation. Model regions that use coal PZ/AMP with CCS include China, Eastern and Western Europe, Japan, Korea and India. Regions that use gas PZ/AMP with CCS include China, the Middle East and North America.

The projected capital-cost trajectories of both CCS technologies are shown in Figure 31. The model can only build small demonstration CCS projects until 2023; after that, the technology is free to be built at scale. The costs decline for both technologies as there are more doublings in capacity. However, the decline reduces, as it is harder for more doublings to occur once the capacity is at a high level. Also, sufficient capacity is built and as it lasts for 50 years, the model stops building new coal and gas PZ/AMP CCS capacity.

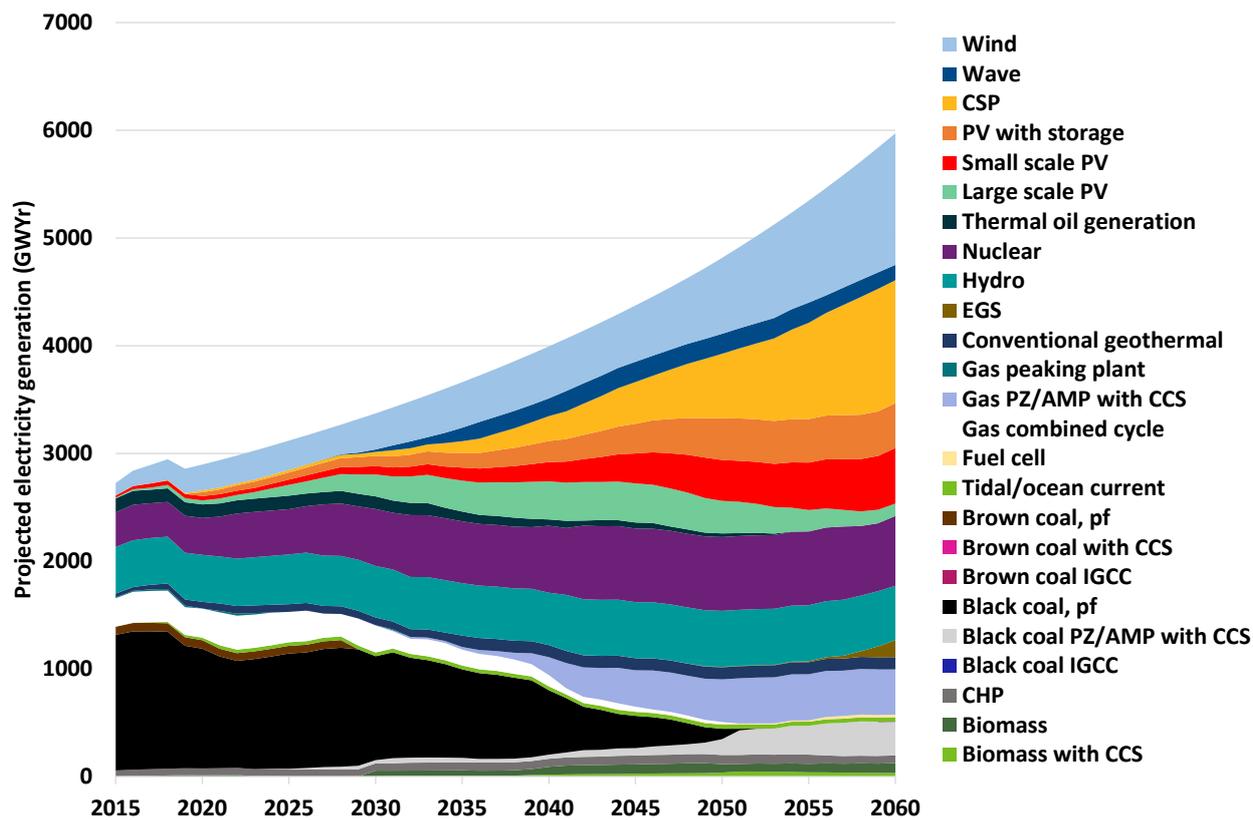


Figure 30 Projected electricity generation under a two-degree carbon-price scenario

CCS = carbon capture and storage; CHP = combined heat and power; CSP = concentrating solar power; EGS = enhanced geothermal system; IGCC = integrated gasification combined-cycle; pf = pulverised fuel; PV = photovoltaic; PZ-AMP = piperazine/amino-methyl-propanol

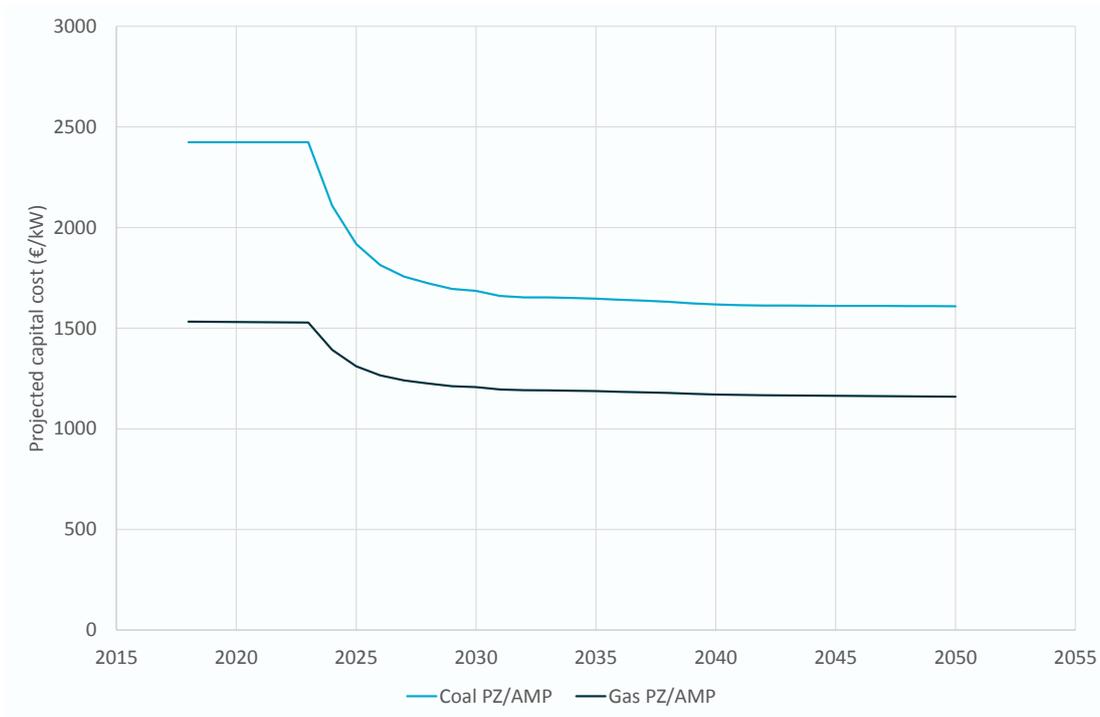


Figure 31 Projected capital cost of coal and gas piperazine/amino-methyl-propanol (PZ/AMP) under a 2-degree carbon-price scenario

The LCOE has been recalculated for coal and gas PZ/AMP in the years 2030 and 2050 to examine the impact of future capital-cost reductions on LCOE. The comparison of these LCOEs with those of 2018 under the three scenarios is shown in Figure 32.

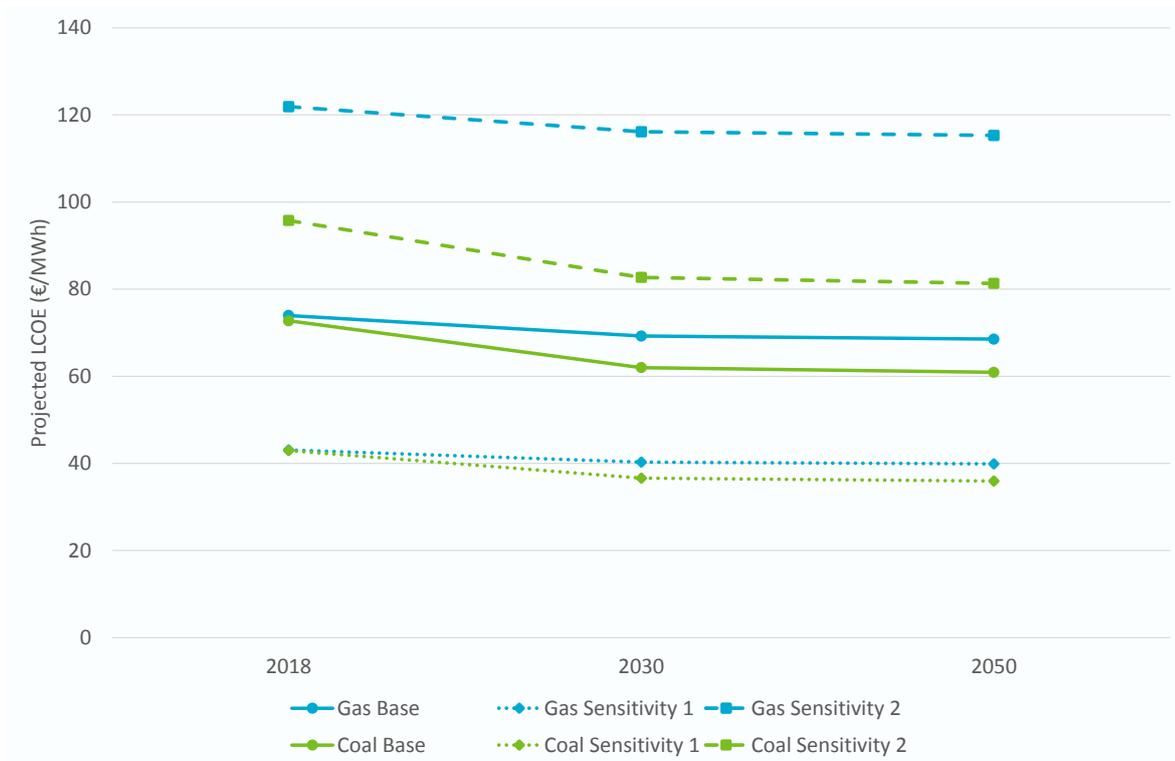


Figure 32 Projected levelised cost of electricity (LCOE) of gas and coal piperazine/amino-methyl-propanol under different scenarios for selected years

The LCOE reduces between 2018 and 2030, and then flattens out from 2030 to 2050, in line with the capital-cost reduction shown in Figure 31. The LCOE of coal reduces more (15%) than that of gas (6%) because the capital-cost reductions are greater for coal than gas. The LCOE of coal technologies is also affected more by the capital cost than for gas technologies, as gas technologies have a higher fuel cost and tend to be affected more by changes to the fuel cost rather than capital cost. This can be seen in the difference between the coal and gas Sensitivity 2 scenario, where the price of fuel is double that of the base scenario; the gas LCOE is ~165% higher compared with the base and the coal LCOE is ~130% higher.

6.5 Evaluation of potential barriers to widespread deployment

In a recent report, Lockwood (2018) assessed the barriers to deployment of CCS technologies. These were found to be similar to any new technology, such as high investment risk and access to commercial financing. While the scale of the projects is comparable to some in the oil and gas industry, oil and gas projects anticipate a high rate of return, which does not exist for CCS projects. The long project lead times, reliance on shared infrastructure, need for legislation around CO₂ storage, and uncertain political and public support are additional challenges for CCS projects. Napp et al. (2014) surveyed 100 representatives from the industry sector to identify opinions on the key barriers to deployment of CCS in the industrial sector. These were determined to be economics, lack of nearby storage sites, and necessity of transport and storage networks.

The investment risk will be highest for initial projects, because they have to finance pipelines and storage themselves, whereas later projects can piggyback off this investment. A potential solution to this issue is to disaggregate the components of CCS, separating the CO₂ emitters from the transport and storage companies. Governments could develop the transport and storage infrastructure (similar to roads and pipelines now). A strength of CCS development has been the high number of research and technology developers working in this area, leading to initiatives and international collaborations around its development and deployment.

High cost is still one of the major barriers to widespread deployment of CCS projects in general. Rubin et al. (2015) evaluated the evolution of cost studies for PCC, oxyfuel and pre-combustion capture plants from 2005–2015. Overall, there has been an increase in the capital cost of CCS facilities, but this cost increase has been offset somewhat by lower annual capital charge factors and higher assumed capacity factors being used. For supercritical pulverised coal (SCPC) plants, the resulting LCOEs are slightly lower than those estimated a decade ago, and are comparable to the LCOE estimated for oxyfuel plant. Previously, IGCC was seen to have a competitive advantage over the other capture technologies for CCS applications due to its higher efficiencies. This view has changed more recently as construction of new coal-based IGCC plant without capture has stalled. LCOEs and CO₂ capture costs of IGCC facilities with CCS are estimated to be slightly higher than for SCPC plants with CCS.

Bui et al. (2018) note that reducing the costs of CCS requires the following:

1. investment in large CO₂ storage hubs, supplying multiple CO₂-production sites connected through large, shared pipelines with high load factors
2. investment in power stations with progressive improvements in CO₂ capture capability
3. a reduction in the cost of project capital through a set of measures to reduce risk for investors

4. exploring synergies with EOR.

Despite the challenges, there are now two commercial-scale CCS facilities operating a coal-based power plant. The success of these projects is in part due to the ability to sell the CO₂ for EOR operations. Further development of these technologies will need to move away from reliance on EOR applications, as they are not available to all power stations, and become less important if oil prices drop. It is important that demonstrations also progress for technologies other than the current aqueous-amine absorbents. This is to ensure a portfolio of technology demonstrations so that the program is robust to a single failure, even though the scale of investments required will lead to prioritisation.

Scale-up of the technologies, both in unit size and in number of units, is important for reducing risk. A strategy of iterative scale-up, where later projects learn from earlier ones and adjust their designs at larger scales, has worked well with solar photovoltaic manufacturing and Danish wind turbines (Nemet et al. 2018).

Most of the technologies in Table 38 have achieved successful pilot-scale demonstration, highlighting that there is no thermodynamic or physical constraint to future scale-up of the technology. Most of the techno-economic evaluations completed have used cost data for currently available components, or components similar to those currently available. The use of existing technology components goes some way to increasing the confidence in the reliability of the cost estimates. This is explored in more detail below for the five technologies assessed in Section 6.3.

Liquid absorbents (30 wt% MEA, PZ/AMP)

Liquid-absorbent-based PCC is likely the lowest risk technology for scale-up, having received significant development in areas other than CCS (e.g. natural-gas processing). There are several companies now offering commercial products, and this is the technology currently being used at the two operating commercial-scale CCS facilities applied to coal-fired power plants. These facilities have built confidence in the ability of equipment suppliers to construct and operate large, single-train capture units (Rubin et al. 2015). There is also greater confidence in the use of new equipment, such as the large rectangular concrete absorber towers that have now been demonstrated at the Boundary Dam facility.

New aqueous-amine absorbents suggest cost benefits compared with the standard 30 wt% MEA (see Part II of this report). Those that have progressed to pilot-scale demonstration are typically based on commercially available amines. Newer technologies using designer amines, however, could face barriers relating to manufacture of the absorbent, and subsequently higher costs, until the industry is developed.

Long-term, pilot-scale evaluation has been used to prepare estimates of degradation rates, and hence cost requirements, as the amines are applied to CO₂ capture under flue-gas conditions. Operation of the Boundary Dam facility, however, has shown that degradation rates can still be higher than anticipated. In addition, operation of TCM in particular has highlighted challenges that can arise from emissions relating to amine-based capture. There are potentially engineering and other solutions to these challenges, but they will need to be met for wide scale deployment of the technology to be realised.

Ca-looping

Ca-looping technologies see early potential for integration with cement plant. When applied to power generators, they have benefits when applied as retrofit, particularly where additional power-generation capacity is also required. When applied to a new-build power station, however, they will see significant competition from standard oxyfuel technologies. They are also less applicable to flue gases with low concentrations of CO₂ (i.e. NGCC). Globally there is currently around 700 GW of coal-fired power generation less than 10 years old (Varro 2018), suggesting there is still significant potential market for retrofit technologies.

Mantripragada and Rubin (2014) evaluated Ca-looping applied to a 650-MW coal-fired power station. This produced 120 t/h of solid waste, or roughly 2,900 t/d. The IEAGHG has considered the deployment of CCS in the cement industry (IEAGHG 2013). In that study, an average-sized European cement plant was determined to have a clinker production rate of 3,000 t/d. This suggests that CO₂ capture from a coal-fired power station via Ca looping could provide the majority of the CaO required for the cement plant. This may limit the market potential for on-sale of spent CaO sorbent.

As noted previously, a large number of the components required for Ca-looping (ASU, CPU, CFB) are already commercially available. The technology is able to piggyback off developments already achieved in fluidised-bed combustion. Abanades et al. (2015) note that the oxy-fired CFB combustor used under calcination conditions is highly developed (TRL 7–8). However, the core of the Ca-looping system – the interconnected carbonator–calciner reactor – is at a lower TRL. There is, however, significant large-scale pilot demonstration being pursued by several research and technology companies. Additional advantages of the Ca-looping concept (IEAGHG 2013, Davison 2014) include:

- low-cost, widely available absorbent (limestone)
- flue gas does not require pre-treatment (SO₂ removal)
- environmentally benign nature of CaCO₃
- opportunities for operation flexibility and load following through stockpiling CaCO₃
- possibility of using waste sorbent in the cement industry.

All of these components lower the barriers to large-scale deployment of Ca-looping technologies. Future experimental work is expected to focus on improving sorbent characteristics and progressing opportunities for further process efficiency.

There are currently no publicly available FEED studies for the Ca-looping process, which leaves some uncertainty around the costs estimated to date. Current cost estimates have made use of other publicly available studies (e.g. for oxyfuel processes) to lower some of the uncertainty relating to final plant costs.

Liquid–liquid separating (DMX process)

It is difficult to comment widely on the potential for scale-up of liquid–liquid separating processes, as pilot-scale evaluation has been limited. Degradation of the absorbent is expected to be zero. The low corrosiveness is also expected to allow the use of lower-cost construction materials. Both of these benefits should assist with scale-up of the technology; however, they still need to be proven through long-term, pilot-scale evaluation treating real process flue-gas streams. Progress should be

achieved in this area shortly with the planned pilot-scale demonstration of the DMX process as part of the VALORCO project. This will give greater confidence in the process stability, and projected economics of a full-scale plant.

As liquid–liquid separating processes typically use a standard liquid-absorbent plant layout, albeit slightly more complicated, this assists the potential for scale-up of this technology. The two currently operating commercial liquid-absorbent plants provide evidence of the availability of technology components at the scale required. The more novel decanting aspects are already used commercially in other applications.

A potential challenge for liquid–liquid separating processes could be the smaller number of research organisations pursuing this technology (e.g. compared with aqueous-amine absorbents). While the DMX process has been licensed to a technology supplier, wider industry involvement has been lower than for other CO₂-capture technologies.

Cost estimates have been prepared, which suggest lower costs than the standard 30 wt% MEA process, and comparable to second-generation, aqueous-amine absorbents. A lack of publicly available FEED studies, however, increases the uncertainty around these estimates.

Solid sorbents (VeloxoTherm)

Solid-sorbent processes receive benefit from the wide range of use and operational experience gained in industries other than CCS (e.g. natural-gas processing). Solid sorbents made from benign or inert materials also have the advantage of no hazardous waste by-products or fugitive emissions from the capture facility. For the VeloxoTherm process in particular, the commercial availability of rotary air pre-heaters of similar scale to those required for CO₂ capture assists in the scale-up of this technology. A challenge is the lack of long-term, pilot-scale evaluation treating a coal flue-gas stream. Commercial rotary air pre-heaters use gas-sealing designs that are insufficient for the separation required for the VeloxoTherm process. The use of novel sealing mechanisms and trapezoidal shape-switching mechanism still require long-term, pilot-scale demonstration. Information on wear rate of the seals when exposed to coal combustion flue gas (particulate) is also required.

Inventys has now received financing for a 30 t/d VeloxoTherm pilot facility to be trialled at the Husky Energy Saskatchewan-based facility. This project has several industry backers, including Shell and BP. Such industry involvement will raise confidence in the technology demonstration. As part of a DOE-sponsored project, a FEED study was completed applying the VeloxoTherm technology to a 550-MW power station. This provides greater certainty in the costs proposed. To meet the targets specified in the techno-economic assessment, however, required larger pressure differentials between cycle steps, including some operation under vacuum that has not yet been demonstrated. Phase 2 of the study was not continued, as it was determined that additional work around adsorbent selection was required to meet DOE targets. Greater confidence in the technology will be acquired once the planned pilot-scale demonstration is completed.

Inventys manufacture the structured solid sorbent in-house. They are currently building a commercial manufacturing line that will have the capability of supplying beds for approximately one 5,000 t/d plant per year. This capacity, once established, will allow them to supply roughly one commercial-scale power plant per year.

Membrane (MTR Polaris)

The membrane processes considered in Section 6.3 were some of the highest-cost technologies for CO₂ capture from coal and gas-fired power plants. One reason for this is that the comparison was completed for 90% capture of CO₂ from the flue gas. As noted previously, membranes show cost benefit when applied at partial capture. This could be useful for early deployment if regulators limit emissions to be comparable to those from NGCC plants. This would only require partial capture from a coal-fired power station. However, recent studies have highlighted the need to progress to capture rates above 90% (IEAGHG 2019). To improve the separation efficiency of membranes when applied to PCC from power stations, processes that enrich the combustion air (i.e. increase flue-gas CO₂ concentration) have been proposed. This, however, increases the complexity of retro-fitting this technology to existing power stations, as modification of coal-boiler gas flow paths is required.

Membranes have already seen commercial deployment in other industries at a similar scale to that required for PCC applications. However, a key point highlighted in the cost analyses completed to date is the lack of reliable and publicly available cost estimates for the membrane units. Currently, cost estimates are taken from other industries, such as reverse osmosis or gas-processing plants. Another unknown for membrane processes is the lifetime of the membrane modules. Current cost estimates assume membrane replacement every 3–5 years. In addition to the scale of the process required when applied to a combustion flue gas, the large and energy-consuming compression equipment required could be costly.

While membranes have seen significant use in other industries, there is currently limited experience integrating several membrane modules in flue-gas streams with vacuum. Despite this, membranes have several attributes that will make them more amenable to stepwise scale-up, such as their low energy requirement and modular nature. Membranes generally see advantage when applied as a bulk removal step; hence, the hybrid concepts that integrate a membrane with another process step show some of the higher predicted cost advantages. FEED studies have been completed applying membrane technologies to coal-fired power plants. Apart from the membrane modules themselves, the balance of plant equipment is readily available.

Membranes have seen significant pilot-scale demonstration, with MTR anticipated to complete evaluation at TCM in the near future. The wide range of research and commercial developers investing in membrane technologies all bode well for future scale-up and deployment.

Oxyfuel gas turbine (Allam cycle)

The Allam cycle was found to be the lowest-cost option when applied to CO₂ removal from natural-gas-based power generation. This technology, however, requires significant technology development, and is thus one of the higher-risk technologies for scale-up of those considered here. In their review of oxyfuel gas turbines, IEAGHG (2015) listed the Allam cycle as having the lowest maturity components of the cycles considered, and still at the level of laboratory scale and material testing. Working with the turbine and heat exchanger manufacturers directly in the scale-up of this technology has gone a long way to de-risking this process. Large-scale demonstration of the technology is still lacking, but will shortly be provided by the 50-MW_{th} demonstration facility currently being commissioned by NET Power in the USA.

Oxyfuel gas turbines are not a retrofit technology. They are an advanced combustion system with advantages when CO₂ capture is required. They are compact in nature, with slightly smaller sizes

than anticipated for NGCC with PCC. There is limited information in the public domain relating to several of the cycles currently being commercialised, which can make estimating costs and future development difficult. In recently completed studies, the IEAGHG estimated only a slight decrease in LCOE for the Allam cycle over NGCC with CCS using a proprietary amine absorbent. More recently, Wood (2018) completed a cost analysis that suggested higher costs for the Allam cycle compared with NGCC with PCC (Cansolv). NET Power reviewed the IEAGHG (2015) report, and suggest that the higher costs anticipated were a result of proprietary information not being publicly available.

7 Conclusions and recommendations

This report has considered current CCS research, development and demonstration of technologies applicable to post-combustion, oxyfuel combustion and pre-combustion capture of CO₂.

Comparison has been made to the previous review, highlighting developmental progression over the past five years. Cost estimates and FEED studies in the literature were reviewed to give insight into potential cost reductions compared with the first-generation CO₂-capture technologies (i.e. 30 wt% MEA). Industry support and investment, and planned and ongoing demonstration activities, were assessed to provide an indication of the likely development trajectory of the various technologies.

The information reviewed has been summarised in the following tables. The TRL of the various technologies is provided, along with comparison to the TRL given in the previous review where applicable. Arrows indicate the development trajectory of the technology as follows:

- An upwards arrow indicates that the technology has commercial backing and/or current or planned larger-scale evaluation/demonstration of the technology is ongoing.
- A sideways arrow indicates that while there may be ongoing pilot-scale demonstration of the technology, there are no current plans for further larger-scale demonstrations.
- A downwards arrow indicates that while some pilot or laboratory-scale evaluation has been achieved, current ongoing research is at a lower scale than that achieved previously.

Finally, a summary of anticipated reductions in LCOE compared with standard CO₂ capture technology has been provided. This is summarised into three categories: Low, LCOE decrease <10%; Medium, 10–30% reduction; High >30% reduction. Table 40 provides results for post-combustion and Ca-looping technologies, Table 41 summarises oxyfuel and CLC, and Table 42 summarises pre-combustion capture technologies.

Table 40 Technology readiness level (TRL), development trajectory and predicted changes to levelised cost of electricity (LCOE) for post-combustion capture and high-temperature solids-looping processes

TECHNOLOGY		TRL AT PREVIOUS REVIEW	CURRENT TRL	CURRENT DEVELOPMENT TRAJECTORY	PREDICTED LCOE DECREASE C.F. STANDARD TECHNOLOGY
Liquid absorbents	Aqueous amine	6–9	6–9	→	Low
	Amino acid and other mixed salts	–	6	↑	Low
	Ionic liquids	1	4	↓	–
	Encapsulated absorbents	1	2–3	→	–
	Water-lean absorbents	–	5	↑	Medium
	Precipitating	4–5	4–6	→	Medium
	Liquid–liquid separating	4	4–5	↑	Low
	Catalysts	1	6	↑	Medium
Membranes	Polymeric membranes	6	6	↑	Low
	Membrane contactors	–	5–6	→	Medium
	Hybrid processes	6	6	↑	Medium
Solid sorbents	Pressure-swing adsorption and temperature–pressure swing adsorption	3	6	→	Medium
	Temperature swing adsorption	1	6	↑	Medium
	Ca looping	6	6	→	Medium
Cooling and liquefaction		3	5	→	Medium
Electrochemical separation		1	4	↑	High
Algae-based capture		1	4	↓	–
Direct air capture		–	5	→	–

Table 41 Technology readiness level (TRL), development trajectory and predicted changes to levelised cost of electricity (LCOE) for oxyfuel and chemical-looping combustion processes

TECHNOLOGY	TRL AT PREVIOUS REVIEW	CURRENT TRL	CURRENT DEVELOPMENT TRAJECTORY	PREDICTED LCOE DECREASE C.F. STANDARD TECHNOLOGY
Pressurised oxyfuel combustion	–	5	→	Medium
Oxyfuel gas turbines	2–5	2–5	↑	Low
High-temperature air-separation membranes	4–7	4–7	→	Low
Chemical-looping combustion	2	4–5	→	Medium

Table 42 Technology readiness level (TRL), development trajectory and predicted changes to levelised cost of electricity (LCOE) for pre-combustion capture processes

TECHNOLOGY	TRL AT PREVIOUS REVIEW	CURRENT TRL	CURRENT DEVELOPMENT TRAJECTORY	PREDICTED LCOE DECREASE C.F. STANDARD TECHNOLOGY
H ₂ -separation membranes	5	5–6	→	Low
CO ₂ -separation membranes	5	5–6	→	Low
Solid sorbents	–	5	→	Low
Chemical liquid absorbents	–	5	→	Low
Sorbent-enhanced water–gas shift	5	4–6	→	Medium
Sorption-enhanced reforming	–	4	→	Low
Clathrates	–	4	→	Low

The tables above highlight that while important, cost is not the only driver for a particular technology to be considered desirable for further development.

Following this assessment, technologies that had progressed through to pilot-scale evaluation were summarised, and a more detailed assessment of their potential for widespread deployment in the next 5–10 years was assessed. To assist with this, a set of metrics were established to provide an indication of the technologies’ attractiveness for further development based on:

- level of demonstration achieved
- potential for cost reduction
- use and experience in industries other than CCS
- availability of components
- ease of retrofit.

A ranking was applied to each assessment category, which allowed an overall score to be calculated for each technology. Scores ranged from 11–18 out of 21 for the 23 technologies evaluated:

- For PCC applications, high scores (above 15/21) were attributed to electrochemical separations, solid sorbents, liquid–liquid separating, mixed salt and water-lean absorbents. These technologies typically ranked higher than others due to application and development achieved in non-CCS industries.
- For oxyfuel combustion technologies, a high score was given to CLC.
- For pre-combustion capture, H₂ and CO₂-separation membranes, solid sorbents and chemical liquid absorbents also scored above 15.

As mentioned previously, a high scoring here is not necessarily an indication of ongoing development potential. An example is oxyfuel gas turbines. These have lower scores, due to the higher level of development required and the lower level of demonstration achieved to date. This will change in the near future with the operation of NET Power’s 50-MW_{th} pilot facility.

Finally, five representative technologies that are receiving ongoing funding for demonstration were selected for a more detailed analysis of their potential to reduce the cost of CCS when applied to

both coal and natural-gas-fired power plant. The technologies evaluated for NGCC plant were Ca-looping, membrane (MTR Polaris), oxyfuel gas turbines (NET Power Allam cycle). These were compared with PCC using standard 30 wt% MEA, and also with a PZ/AMP blend, a generic second-generation absorbent detailed in Part II of this report. For coal-fired plants, the technologies evaluated included Ca-looping, membrane (MTR Polaris), liquid–liquid separating (IFPEN DMX), solid sorbent (Inventys VeloxoTherm), PZ/AMP and MEA. For most technologies, information on cost was taken from publicly available economic analysis. For MEA and PZ/AMP, cost information was taken from Part II of this report. The results are summarised as follows:

- Of the gas-fired technologies, the Allam cycle is the lowest in cost and captures more emissions than the other technologies. PZ/AMP is the lowest-cost coal-fired technology. Membrane is the most expensive technology for both fuel types.
- Unit size has minimal impact on the LCOE, and the impact is greater for coal-fired technologies.
- Changes to fuel cost, discount rate, plant life and CO₂ transport and storage costs, as explored through the sensitivity scenarios, have a significant impact on the LCOE, but this is fairly uniform across technologies. The impact is greater for gas-fired technologies; in the order of ±50% compared with ±30% for coal-fired technologies.
- Under the base scenario, the CO₂-capture cost and CO₂-avoidance costs are below ~100 €/tCO₂ for gas-fired and below ~60 €/tCO₂ for coal-fired technologies. These costs are within the range of future carbon-price trajectories; thus, with such a carbon price in place, these technologies would be cost-effective.

CSIRO's GALLM-E model was used to project the future cost of electricity-generation technologies, and updated to include the new baseline technology, PZ/AMP. By 2030, the LCOE for PZ/AMP is projected to decrease in cost by 15% for coal-fired and 6% for gas-fired power plants. Lastly, the barriers to widespread deployment of the technologies were assessed. For most technologies, larger-scale FEED studies have made as much use as possible of currently available components. Where this is not possible, collaboration with industry and technology suppliers has de-risked the process as much as possible. This highlights that the technological barriers to widespread deployment are being addressed. Of greater hindrance are likely elements that will be experienced for most large-scale CCS projects: high commercial risk and investment cost, particularly when EOR options are not available for revenue from CO₂ sales. Additional challenges for CCS projects include the need for legislation around CO₂ storage, and uncertain political and public support.

This report suggests the following recommendations:

- Long-term, pilot-scale evaluation treating real process flue-gas streams is required to build confidence in any new technology. Information gathered from these demonstrations should be used to update techno-economic analyses.
- It is important that demonstrations progress for a range of technologies. This is to ensure a portfolio of technology demonstrations so that the program is robust to a single failure. In addition, choice of technology options will increase competition and cost reduction.

- The costs of different technologies must be compared over a consistent baseline. Wider sharing of FEED studies and cost estimates will also build confidence in results being reported.
- The current baseline for comparing new technologies needs updating. Almost all technologies now see a cost benefit compared with the previous standard (30 wt% MEA). A new baseline proposed here, a generic and publicly available PZ/AMP blend, has anticipated costs comparable to or below current, emerging technologies.

Appendix A Economic parameters

Table A.1 Parameters used for levelised cost of electricity calculation for gas-fired technologies

PARAMETER	UNIT	ALLAM CYCLE	CA LOOPING	MEMBRANE	PZ/AMP	MEA	NO CCS
Unit size	MW _{net}	855	807	604	761	728	882
Capital expenditure (capex)	€/kW	1192	1118	1988	1532	1611	1038
Fixed operating expenditure (opex)	€/kW/year	40	31	99 ²	52	55	34
Variable opex	€/kW/year	9	430 ¹	5	12	16	4
Total opex	€/kW/year	–	–	–	–	–	–
Efficiency	% LHV	54	–	48	51	49	59
Emissions	kg/kWh	0.006	0.036	0.043	0.040	0.042	0.35
CO ₂ to store	kg/kWh	0.33	0.33	0.39	0.36	0.38	0
Capture rate	%	98.2	90	90	90	90	0
Capacity factor	%	85	85	85	85	85	85
References		(White & Weiland, 2018) (IEAGHG, 2015)	(Hu & Ahn, 2017)	(van der Spek et al. , 2018)	This study	This study	This study

¹Includes the fuel cost. An efficiency was not provided, so it was not possible to separately calculate a fuel and variable O&M cost without fuel.

²Includes the membrane cost. This was to be paid every six years, but in this case it has been converted into an annual payment.

Table A.2 Parameters used for levelised cost of electricity calculation for coal-fired technologies

PARAMETER	UNIT	CA LOOPING	MEMBRANE	VELOXOTHERM	DMX	PZ/AMP	MEA	NO CCS
Unit size	MW _{net}	886	550	560	592	684	634	817
Capital expenditure (capex)	€/kW	2128	3002	2221	3524	2424	2654	1819
Fixed operating expenditure (opex)	€/kW/year	–	80	75	66	67	73	50
Variable opex	€/kW/year	–	75	67	13	26	32	9
Total opex	€/kW/year	131	–	–	–	–	–	–
Efficiency	% LHV	33	32	32	36	37	34	44
Emissions	kg/kWh	0.097	0.10	0.081	0.063	0.084	0.095	0.74
CO ₂ to store	kg/kWh	0.87	0.93	0.73	0.72	0.76	0.86	0
Capture rate	%	90	90	90	90	90	90	90
Capacity factor	%	85	85	85	85	85	85	85
References		(Mantripragada & Rubin, 2014) (Hanak & Manovic, 2017) (Rolfe, et al., 2017) (Rolfe, et al., 2018) (Abanades, et al., 2015)	(NETL, 2012) (Merkel et al., 2016)	(NRG Energy, 2016)	(Broutin et al., 2017)	This study	This study	This study

Table A.3 Summary of assumptions used in literature cost studies used in LCOE calculations for natural gas-fired technologies

TECHNOLOGY	NO CCS MEA AMP/PZ	ALLAM CYCLE	ALLAM CYCLE	CA LOOPING (WITH EXHAUST GAS RECYCLE)	MEMBRANE (WITH EXHAUST GAS RECYCLE)
Reference	This study	IEAGHG 2015	White and Weiland 2018	Hu and Ahn 2017	van der Spek et al. 2018
Cost methodology followed	IEAGHG	IEAGHG	NETL 2011	DOE/NETL 2013 followed for reference NGCC plant. Detailed information on economic assumptions not provided.	European benchmarking task force for NGCC design. Cost based on methodology of Rubin et al. 2013
Fuel	Natural Gas 7 MPa 51.47 MJ/kg HHV	Natural Gas 7 MPa 51.47 MJ/kg HHV	Natural Gas 3 MPa 52.6 MJ/kg HHV	Natural Gas	Natural gas 51.47 MJ/kg HHV
Plant location	Greenfield location The Netherlands	Greenfield location The Netherlands	Greenfield site Mid-west USA		Rotterdam, The Netherlands
Cooling system	Mechanical/natural draft cooling towers	Natural draft cooling tower	Mechanical draft evaporative cooling tower		
Total plant cost	Installed costs + engineering contractor's fees + contingencies	Direct materials + construction + other costs + EPC services + contingency	Equipment + Installation + contractor's fees + contingencies		
Installed costs, Bare erected cost	Equipment costs + materials costs + labour costs	Based on in-house data	Equipment and supporting facility costs, direct and indirect labour		
Engineering contractor's fees	10% of installed costs	Based on in-house data	8-10% of Bare erected cost		
Project contingency	10% of (installed costs + engineering contractor's fees)	10% of Total installed cost	15% (bare erected cost + Engineering contractor's fees + Process contingency)		40% of Total installed costs
Process contingency (CCS only)	16% of (installed costs + engineering contractor's fees)	Not included	20% on CCS facility 5% on instrumentation and controls		
Total Capital requirement (Total Investment cost, Total overnight cost)	Total plant cost + owners costs + spare parts + start-up costs	Total plant cost + interest during construction + spare parts + working capital + start-up costs + owners costs	Total plant cost + owners costs		
Owners costs and fees	7% of Total plant cost	7% of Total plant cost	15% of Total plant cost		Not included

Spare parts	0.5% of Total plant cost	0.5% of Total plant cost	0.5% of Total plant cost	
land			\$3000/acre (100 acres)	
Interest during construction		8%		Not included
Financing cost			2.7% of Total plant cost	
Start-up costs				Taken from Lew et al. based on number of hot/cold/warm start-ups
Maintenance, operating and support labour costs	3 months	3 months	6 months	
Maintenance materials	1 month	1 month	1 month	
Chemicals, consumables and waste disposal costs	1 month	1 month	1 month	
Fuel cost	25% of 1 month	25% of 1 month	25% of 1 month	
Modifications	2% of Total plant cost	2% of Total plant cost	2% of Total plant cost	
Construction time	3 years	3 years	3 years	3 years
Capital expenditure schedule	20%/45%/35% of Total plant cost, year 1 – 3	20%/45%/35% of Total plant cost, year 1 – 3	10%/60%/30% of Total plant cost, year 1 – 3	
Fixed operating costs				
Maintenance costs, materials, labour	2.2% of total plant cost per year	2.5% Total plant cost for novel technologies 1.5% Total plant cost for other units	Weighted analysis	3% of Total plant cost per year
Maintenance materials, labour	60%, 40% of maintenance costs	60%, 40% of maintenance costs	Weighted analysis	
Operating labour	60 k€/person-year	60 k€/person-year	39.70/hr Associated burden labour 30% base labour rate	Taken from EBTF
Admin./support labour	30% of operating + 12% of maintenance cost	30% of operating + 12% of maintenance cost	25% of burdened O&M labour	
Insurance, local taxes and fees	1% of Total plant cost	1% of Total plant cost	2% of Total plant cost	2% of Total plant cost per year

Table A.4 Summary of assumptions used in literature cost studies used in LCOE calculations for coal-fired technologies

TECHNOLOGY	NO CCS MEA AMP/PZ	CA LOOPING	CA LOOPING	CA LOOPING	CA LOOPING	DMX	VELOXOTHERM	MEMBRANE	MEMBRANE
Reference	This study	Mantripragada and Rubin 2014	Hanak and Manovic 2017	Rolfe et al. 2017 Rolfe et al. 2018	Abanades et al. 2015	Broutin et al. 2017	NRG Energy 2016	Merkel et al. 2016	NETL 2012
Cost methodology followed	IEAGHG			EU best practice guidelines		EU best practice guidelines	NETL 2013	NETL 2010	NETL 2010
Fuel	Bituminous 27.1 MJ/kg HHV	Coal 30.5 MJ/kg HHV	Coal	Coal 25.4 MJ/kg LHV	Coal	Bituminous 25.2 MJ/kg LHV	Bituminous 27.1 MJ/kg HHV	Bituminous 27.1 MJ/kg HHV	Bituminous 27.1 MJ/kg HHV
Plant location	Greenfield location The Netherlands	Retrofit USA	Retrofit Europe	Retrofit	Retrofit	Europe	Greenfield site Mid-west USA	Greenfield site Mid-west USA	Greenfield site Mid-west USA
Cooling system	Mechanical/natural draft cooling towers					Natural draft cooling tower	Mechanical draft cooling tower	Mechanical draft cooling tower	Mechanical draft cooling tower
Total plant cost	Installed costs + engineering contractor's fees + contingencies						Equipment + Installation + contractor's fees + contingencies	Equipment + Installation + contractor's fees + contingencies	Equipment + Installation + contractor's fees + contingencies
Installed costs, Bare erected cost	Equipment costs + materials costs + labour costs		Capital cost from correlation	In-house simulation in ECLIPSE	Estimated from DOE/NETL 2010, ZEP 2011, IEA 2008		Vendor quotes and scaled from DOE/NETL baseline report	Boiler cost increased 10% to account for incorporation of MTR system	Vendor quotes, scaled estimates
Engineering contractor's fees	10% of installed costs	7% direct capital cost					8-10% of Bare erected cost	8-10% of Bare erected cost	8-10% of Bare erected cost
Project contingency	10% of (installed costs + engineering contractor's fees)	22% direct capital cost		10% of Total capital investment			15-30% (bare erected cost + Engineering contractor's fees + Process contingency)	15-30% (bare erected cost + Engineering contractor's fees + Process contingency)	15-30% (bare erected cost + Engineering contractor's fees + Process contingency)

Process contingency (CCS only)	16% of (installed costs + engineering contractor's fees)	21% direct capital cost		20% applied to novel technology	20% applied to membrane system 15% applied to CPU	20% applied to CCS facility
Royalty fees		5% direct capital cost		Not included	Not included	Not included
General facilities capital		10% direct capital cost				
Indirect costs				14% of Total direct plant costs		
Total Capital requirement (Total Investment cost, Total overnight cost)	Total plant cost + owners costs + spare parts + start-up costs					
Owners costs and fees	7% of Total plant cost		15% of Engineering procurement and construction	15% (Total direct plant costs + indirect costs) Includes contingencies	15% Total plant cost	15% Total plant cost
Spare parts	0.5% of Total plant cost				0.5% of Total plant cost	0.5% of Total plant cost
land					\$3000/acre (300 acres)	\$3000/acre (300 acres)
Inventory capital					60 days fuel and consumables	60 days fuel and consumables
Financing cost					2.7% Total plant cost	2.7% Total plant cost
Start-up costs						
Maintenance, operating and support labour costs	3 months				6 months	6 months

Maintenance materials	1 month			1 month	1 month	1 month
Chemicals, consumables and waste disposal costs	1 month			1 month	1 month	1 month
Fuel cost	25% of 1 month			25% of 1 month	25% of 1 month	25% of 1 month
Modifications	2% of Total plant cost			2% of Total plant cost	2% of Total plant cost	2% of Total plant cost
Construction time	3 years	3 years	4 years	5 years	5 years	5 years
Capital expenditure schedule	20%/45%/35% of Total plant cost, year 1 – 3	20%/45%/35% of Total plant cost, year 1 – 3	20%/30%/30%/20% of Total plant cost, year 1 – 4	10%/30%/25%/20%/15% of Total plant cost, year 1 – 5	10%/30%/25%/20%/15% of Total plant cost, year 1 – 5	10%/30%/25%/20%/15% of Total plant cost, year 1 – 5
Fixed operating costs						
Maintenance costs, materials, labour	2.2% of total plant cost per year	1% of total plant cost per year	2.5% EPC cost per year	Weighted analysis	Weighted analysis	Weighted analysis
Maintenance materials, labour	60%, 40% of maintenance costs	1% of total plant cost per year		Weighted analysis	Weighted analysis	Weighted analysis
Operating labour	60 k€/person-year		1% EPC cost per year	39.70/hr, 50 h/week Associated burden labour 30% base labour rate	34.65/hr, 50 h/week Associated burden labour 30% base labour rate	34.65/hr, 50 h/week Associated burden labour 30% base labour rate
Admin./support labour	30% of operating + 12% of maintenance cost			25% of burdened O&M labour	25% of burdened O&M labour	25% of burdened O&M labour
Insurance, local taxes and fees	1% of Total plant cost	1.5% of Total capital investment		2% of total plant cost	2% of total plant cost	2% of total plant cost

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Part II Update on the post-combustion CO₂-capture benchmark technology

8 Performance of commercially available, amine-based, post-combustion capture technologies

Many studies have taken chemical absorption with 30 wt% monoethanolamine (MEA) solutions as the benchmark technology for CO₂ capture applications. Progress in amine-based, post-combustion CO₂ capture (PCC) is such that current commercially available technologies will have significantly better performance than this baseline. In this report, the technology characteristics that underlie the improved performance of advanced, amine-based processes have been investigated and enabled the definition of the performance of a new benchmark technology. The aim was not to select the best technology among the available commercial options, but rather define an 'open-source' technology that lends itself to independent analysis and comparison.

The work has resulted in the definition of a technology that reflects the performance of current state-of-the-art PCC technologies, as described below.

8.1 Performance definition for amine-based PCC processes

The performance of an amine-based PCC plant can be expressed along three axes:

1. Energy performance

PCC processes require additional energy for the separation and compression process and this leads to an additional energy requirement and consequential additional resource consumption, which is undesirable. In the case of power plants, this translates to a lower output and reduced energy conversion efficiency.

2. Environmental performance

PCC as part of a larger carbon capture and storage (CCS) chain is essentially an emission-reduction technology that should have minimal environmental impacts. However, the use of amines that degrade in flue gas service generates waste streams that are often treated as chemical wastes. Emissions of amine and reaction by-products to the atmosphere are also a cause of concern.

3. Economic performance

The implementation of PCC in power plants needs to be competitive with other low-emission technologies, which have seen drastic cost reductions in recent years. The additional capital and operational costs of a PCC plant will increase the cost of generation, and this needs to be minimised.

The performance of the PCC process is ultimately derived from a series of characteristics, which are described in the next section.

8.2 Performance characteristics for amine-based PCC processes

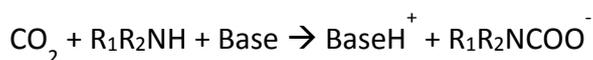
The performance of an amine-based PCC process is determined by three classes of characteristics: performance characteristics of the amines used in the absorption liquid, energy performance, and process and equipment. Each of these is described below.

1. Performance characteristics of the amines used in the absorption liquid

The characteristics relevant to the amines used are:

- *Amine formulation in absorption liquids*

Amines are mostly deployed in formulated, aqueous solutions, often containing more than one amine. The formation of a carbamate through the reaction with CO₂ with the consequential release of a proton provides a high mass-transfer rate and is considered to be the main reaction pathway in all commercial technologies. The general reaction pathway can be described as follows:



Where R₁ = an alkyl/alkanol substituent and R₂ = H or an alkyl/alkanol substituent.

The base can be the amine itself (R₁R₂NH), other amines or another alkaline component, such as carbonate. Carbamates are formed by primary or secondary amines, provided there is no sterical hindrance. Ideally one wants to maintain the solution reactivity at a high level, and the choice of the base is such that the proton will react preferentially with the base rather than with the carbamate-forming amine. In practice, the reaction chemistry is more complicated, particularly where it concerns di-amines, such as piperazine. Amine formulations might also contain corrosion inhibitors or oxygen scavengers.

- *Amine consumption*

The amine used in the capture process will be consumed over time through:

- Physical losses, e.g. through evaporation, droplets and aerosols. In addition to these absorber losses, amines might also be lost through accidental spills. The amine vapour pressure over the amine solution will affect the losses through the absorber exhaust and health risks associated with a spill.
- Chemical losses through oxidative or thermal degradation, or reactions with other flue gas constituents, such as SO_x or NO_x. These degradation products and by-products can also be emitted to the atmosphere and reduce local air quality.

Amine consumption is usually expressed in kg/tonne CO₂ captured, with the amine being replenished on a regular basis as determined by the maintenance routine. The amine consumption is not only determined by amine characteristics, such as vapour pressure in aqueous solutions and its chemical stability, but can also be limited by the process design. Multiple flue-gas wash sections can reduce the physical losses, and the amines can be separated from their degradation products with a reclaimer.

- *Physical and chemical properties of amines in solution*

The physical properties of amine solution have a variety of effects on process performance. The viscosity and density will affect the absorber column design and CO₂ mass transfer. In particular, the viscosity is strongly affected by the CO₂ loading of the solution, and will also affect heat transfer in the heat exchangers. The heat capacity of the solution will be important, as it constitutes an important contribution to the heat requirement for regeneration.

An important chemical property is the pKa value of the amine, as there is strong link with the reactivity towards CO₂. Amines also need to be stable in the presence of oxygen and metal surfaces, and have high decomposition temperatures.

- *Amine costs*

While not a technical parameter, the costs for the individual amine are an important consideration. Cost is a reflection of the amine availability and therefore its propensity to be introduced quickly into the applications market of large-scale CCS systems.

- *Ecotoxicity and biodegradability*

The use of amines will be subject to permitting processes that will require assessment to determine any harmful environmental impacts. This means that amines will need to be subject to protocols that assess their toxicity in the environment and propensity to degrade in the environment.

2. Energy performance

The energy requirement for amine-based PCC is a crucial property, particularly in power plants, where output will be significantly reduced when significant amounts of CO₂ are captured. The energy requirement is both thermal, for regeneration of the amine solution, and electrical, for fans and pumps. It can be expressed by the following parameters:

- *Specific thermal energy consumption*

This is the heat required for amine regeneration per unit of CO₂ captured (GJ_{th}/tonne CO₂ or MJ_{th}/kg CO₂). Heat is normally extracted as steam from the power plant, and is consequently not used for power generation. Heat might also be externally sourced from a separate combustion unit.

- *Specific electrical-energy consumption*

This is the electricity consumption per unit of CO₂ captured (GJ_e/tonne CO₂ or MJ_e/kg CO₂) needed for rotating equipment, such as fans, pumps and compressors used in the capture process. It also incorporates compression or liquefaction of CO₂. Finally, the electricity consumption to meet the cooling requirements of the capture process needs to be considered.

- *Specific equivalent electrical-energy consumption*

This is a measure of the overall energy requirement of the capture process, expressed as electricity consumption per unit of CO₂ captured (GJ_e/tonne CO₂ or MJ_e/kg CO₂). It is the sum of the specific electrical-energy consumption and the equivalent electrical-energy requirement for the thermal energy used for regeneration of the amine solution. If the heat is extracted from the power plant steam cycle, it is equivalent to the reduction in power plant output. This property is therefore influenced by the way the capture plant is integrated with the power station.

3. Process and equipment

The CO₂-capture process and the equipment used can be characterised by the following parameters:

- *Specific absorption liquid flow rate*

This represents the amount of absorption liquid needed per unit of CO₂ captured (m³/tonne CO₂ or l/kg CO₂). It will determine the size of heat exchangers and pumps used and the desorber size to a large extent.

- *Specific absorber capacity*

This is the packing volume per rate of CO₂ capture in m³/(tonne/h). It can be understood as a measure of the productivity of the absorption process, and is determined by the mass transfer, the driving force and the specific surface area of the packing.

- *Process design*

The conventional process design for a CO₂-capture process has undergone considerable developments, with a range of new, more energy-efficient designs now available. Examples include absorber intercooling, split flow and lean vapour recompression. These have been reviewed in a previous IEAGHG study (2014).

- *Materials of construction and amine corrosivity*

Liquid absorption PCC processes located at a power generating plant will likely be large. Utilising lower cost construction materials will be important for minimising cost. This will be affected by the particulars of the process, including the corrosivity of the amine. Lower cost construction methods are already being employed, including the use of concrete columns for the absorber.

- *Temperature of regeneration*

The specific amine used for the CO₂ capture process will influence the temperature and pressure that can be used for regeneration. This will impact on the level of steam or waste heat that will be required by the PCC process for the regeneration step.

- *Process emissions*

These are a significant factor for the environmental footprint of PCC systems, as a result of the large-volume flows. The emissions constitute the amines used and degradation products, such as ammonia, which is an often encountered degradation product. Process emissions are usually expressed in ppm (volume) or mg/Nm³. They are determined by the intrinsic properties of the amine used and the emission control systems, e.g. the wash stages post-absorber.

8.3 Commercially available PCC technologies

This report focuses on the overall technical performance and characteristics of the commercially available amine-based PCC processes, as this essentially underpins the energy, environmental and economic performance. These processes are still to make an impact in terms of global CO₂-emission reductions, but have now been deployed in two power plants on a large scale (around 1 M tonne/annum CO₂) in the Boundary Dam and Petra Nova project. These are ‘first-of-a-kind’ projects for the technology suppliers involved, realised with government grants, and therefore produce CO₂ under semi-commercial conditions. It is anticipated that other technology suppliers would be able to supply suitable PCC technology in the near future. For the objectives in this study, commercial availability is therefore defined as the technology being, or having been:

- as a minimum, demonstrated in a pilot plant under realistic conditions, i.e. with real flue gases and preferably on a larger scale
- developed by a vendor that is able to supply the technology independently, or in partnership with others at a scale relevant to emissions reduction from power plants or other industrial facilities
- the subject of scale-up studies, i.e. feasibility or front-end engineering design (FEED) studies that provide an insight into overall costs.

PCC technology has been developed by all major suppliers of power plant equipment, suppliers to the oil and gas industry, and some large engineering companies. Several smaller companies have also developed technology that can be scaled up as needed for significant emission reductions from power stations. Performance information from these vendor technologies is not necessarily accessible, due to its proprietary nature. However, most vendors provide results from their technology development on a regular basis, and performance information can sometimes also be derived from information disclosed through feasibility and FEED studies. This report has only considered sources available in the public domain.

A long list of technology suppliers was developed, all of which are considered to be capable of delivering large-scale, commercial PCC plants in the next 10 years. Only two have actually realised a full-scale plant, i.e. a plant that will significantly reduce the emissions of a fossil-fuel fired power station. Other technology suppliers might have demonstrated the technology at a demonstration scale (e.g. at the Technology Centre Mongstad) or have equivalent commercial-scale experience (e.g. with production of food-grade CO₂, or urea

or methanol production). Some technology suppliers might only have evaluated the technology at pilot-plant scale, but have carried out several feasibility studies that provide a pathway towards commercial-scale deployment at medium or large scale. Table 43 provides an overview of the long list of technology suppliers for which information was available in the literature.

Table 43 Long list of technology suppliers capable of delivering large-scale, commercial PCC plants in the next 10 years; blue shading indicates level of current experience

TECHNOLOGY SUPPLIER	PILOT PLANT OR SMALL-SCALE COMMERCIAL PLANTS <100 TONNE CO ₂ PER DAY)	DEMONSTRATION PLANT OR MEDIUM-SCALE COMMERCIAL PLANTS (100–1000 TONNE CO ₂ PER DAY)	COMMERCIAL PLANT AT POWER-PLANT SCALE (>1000 TONNE CO ₂ PER DAY)
Mitsubishi Heavy Industries			
Shell Cansolv			
Fluor			
Aker Solutions			
GE – Ammonia			
ION Engineering			
Carbon Clean Solutions			
BASF-Linde			
China Huaneng			
Toshiba			
IHI			
Hitachi			
Chiyoda			
Siemens			
GE – Amine			
Babcock & Wilcox			
HTC Purenergy			
Prosernat			
CO ₂ Solutions			

8.4 Performance of commercially available PCC technologies

As the next step, the literature study focused on the gathering of information and data on the performance characteristics of the commercially available PCC technologies. The activity used information presented in publications and reports available in the public domain, in many instances authored by the technology suppliers themselves. Most detailed information on the performance characteristics appeared to be available for the larger technology suppliers. For seven technology suppliers, the information is provided in Appendix B.

A comparative overview based on five performance characteristics – reboiler duty, absorption liquid flow rate, electricity consumption, amine/ammonia emission and amine consumption – is provided in Table 44. This comparison is not on the same basis across all technologies, as the data have been derived from different pilot plant or demonstration plants and for different clients. A true comparison is only possible for the same flue gas for each technology supplier and their proprietary amine and process design, but this is not possible in practice from the literature data currently available in the public domain. This will be achieved in practice for large scale projects as on-site comparison of licensed technologies is often performed during early stage FEED or pre-FEED assessments. Such commercially sensitive information however is typically not shared publicly.

It is important to note that commercial technology developers were not approached to assist with this assessment. We recognise that the most up-to-date information on commercial technologies is often not shared publicly. However for the purpose of this review, identifying the performance targets for the proposed new benchmark, the information available in the public domain was deemed to be sufficient.

The overview does provide a good indication for some of the current performances reported, in particular for reboiler duty. It appears that for application in coal-fired power stations, a specific reboiler duty of ~ 2.5 GJ/tonne CO₂ is achievable, whereas for gas-fired combined cycles, specific reboiler duty would be ~ 3.0 GJ/tonne CO₂.

With the exception of Fluor, the composition of the absorption liquid is unknown. Fluor uses a formulation that is based on monoethanolamine in their Econamine FG process. The lack of information on the amine formulation prohibits a detailed validation of the performances reported by the technology suppliers. Moreover, technology suppliers use different proprietary process designs to achieve optimum performance from a given amine formulation. Technology licensors can often adapt their design offering based on the specifics of a project such as CO₂ concentration and the relative value of power versus low pressure steam availability. Variations include the addition or removal of absorber inter-cooling, mechanical vapour recompression, and occasionally split-flow (semi-lean) schemes. Technology suppliers also have different design features to limit amine and ammonia emissions. The consumption of amines in service will be dependent on the type of amine and the reclaiming process used. Reclaiming technologies are also a subject of differentiation between the technology suppliers.

Given the large diversity in amine processes offered by the technology suppliers, and the limited, large-scale deployment expertise, we decided not to select one particular vendor technology as the baseline. Instead, the study focused on selecting several amine formulations for which sufficient information was available and for which process simulations could be carried out.

Table 44 Comparative overview of amine-based, post-combustion CO₂-capture technologies

PARAMETER	REBOILER DUTY	ABSORPTION LIQUID FLOW	ELECTRICITY CONSUMPTION	AMINE/AMMONIA IN EXHAUST	AMINE CONSUMPTION
	GJ/tCO ₂	m ³ /tCO ₂	kWh/tCO ₂	ppm	kg/tCO ₂
Mitsubishi Heavy Industries	2.6 (coal)	10 (coal)	77 (coal)	Amine: 0.7–3 Ammonia: 0.3–2.0	0.35
Shell Cansolv	2.2–2.8 (coal) 2.3–2.9 (gas)	10–16	70 (coal) 100 (gas)	Not found	0.1
Fluor	3.2 (coal) 3.6 (gas)	17	38–40 (coal) 53–125 (gas)	Amine: 0.1–1.0 Ammonia: 1.3–2.2	1.6
Aker Solutions	2.8 (9% CO ₂) 3.4 (gas)	11.4–14.2	Not found	Amine: 0.02 Ammonia: 0.1	0.2–0.6
BASF-Linde	2.7 (coal)	Not found	22	Amine: 0.3–0.5	0.3
Toshiba	2.4–2.6 (coal)	17	Not found	Not found	Not found
Hitachi	2.4 (coal)	Not found	Not found	Not found	Not found

8.5 Liquid-absorbent PCC simulations using different amine formulations

Initial PCC process simulations using ProTreat[®] were carried out for a several amine formulations with a PCC plant that was designed for 90% CO₂ capture. Inlet flue gas properties were taken from the ultra-supercritical pulverised coal (USCPC) power plant simulation with 20% over-fire air, and the natural gas combined-cycle (NGCC) simulation with no flue gas recycle, as described in Appendix C. As both flue gases were at temperatures higher than typical liquid-absorbent plant operating temperatures, a direct contact cooler was added. A blower was placed upstream of the cooler, increasing the pressure to 108 kPa-a at this point. Table 45 provides the flue gas properties entering the PCC plant (before the cooler) and entering the PCC absorber (after the cooler).

Table 45 Flue gas properties used in post-combustion capture process simulations in ultra-supercritical pulverised coal (USCPC) and natural gas combined-cycle (NGCC) power plants

PROPERTY	USCPC	USCPC	NGCC	NGCC
	INLET TO PCC PLANT	INLET TO ABSORBER	INLET TO PCC PLANT	INLET TO ABSORBER
Flue gas flow rate, kg/s	826.8	799.3	1319.8	1307.8
No. trains	3	3	4	4
Flue gas flow per train, kg/s	275.6	266.4	329.9	326.9
Flue gas flow per train, kmol/s	9.47	8.96	11.65	11.48
Temperature, °C	50	40	85.2	39.9
Pressure, kPa-a	101.8	106.2	101.8	106.1
H ₂ O, mol%	12.1	7.1	8.5	7.2
CO ₂ , mol%	13.4	14.2	4.2	4.3
N ₂ , mol%	70.4	74.4	74.4	75.5
NO, mol%	0.8	0.9	0.9	0.9
O ₂ , mol%	3.3	3.5	12	12.2

A range of different liquid absorbents, including 30 wt% monoethanolamine (MEA), were considered for the PCC process. The study focused on liquid absorbents that are widely available, have widely available data, and whose properties are already incorporated into most commercially available simulation software.

An initial improvement to the baseline MEA process is to simply increase the MEA concentration. The HiCapt+ process developed by French Petroleum Institute Energies Nouvelles employs a 40 wt% MEA solution with inhibitors to limit corrosion (Lemaire et al. 2011, Lemaire et al. 2014). A 40 wt% MEA solution has also been evaluated at the Technology Centre Mongstad (Brigman et al. 2014). Activated methyl-diethanolamine (MDEA) solutions (i.e. a piperazine (PZ) and MDEA blend) are widely used in the natural gas processing industry for CO₂ removal. More recently, PZ-MDEA blends have also received interest in CO₂-capture

applications (Dubois and Thomas, 2017; Dubois and Thomas, 2018). As part of the EU-sponsored CESAR project, a blend of amino-methyl-propanol (AMP) and PZ was evaluated (28 wt% AMP, 17 wt% PZ) (Mangalapally and Hasse, 2011). This blend was also evaluated on the Esbjerg CO₂-capture pilot plant (Knudsen et al. 2011) and found to have superior energy performance compared with the baseline 30 wt% MEA. PZ, MDEA and AMP are also found to have better oxidative and thermal stability than MEA, which is a significant advantage in PCC applications (Voice, 2013).

The specific blends evaluated as part of this study are summarised below:

- 30 wt% MEA
- 40 wt% MEA
- 1.5 mol/L (13 wt%) PZ with 3.0 mol/L (27 wt%) AMP
- 17 wt% PZ with 28 wt% AMP
- 10 wt% PZ with 30 wt% MDEA
- 16 wt% PZ with 24 wt% MDEA
- 20 wt% PZ with 40 wt% MDEA.

The absorber and stripping columns were sized to 80% of flooding capacity. For the range of absorbents considered, the effect of altering liquid-to-gas mass flow rate (L/G) ratio on the specific reboiler duty required to capture 90% of the CO₂ was investigated. The effect of two process modifications (absorber intercooling (IC) and rich split (RS)) was also evaluated, to represent the energy-saving designs that most vendors use. These results for the USCPC plant are provided in Figure 33, and for the NGCC plant in Figure 34.

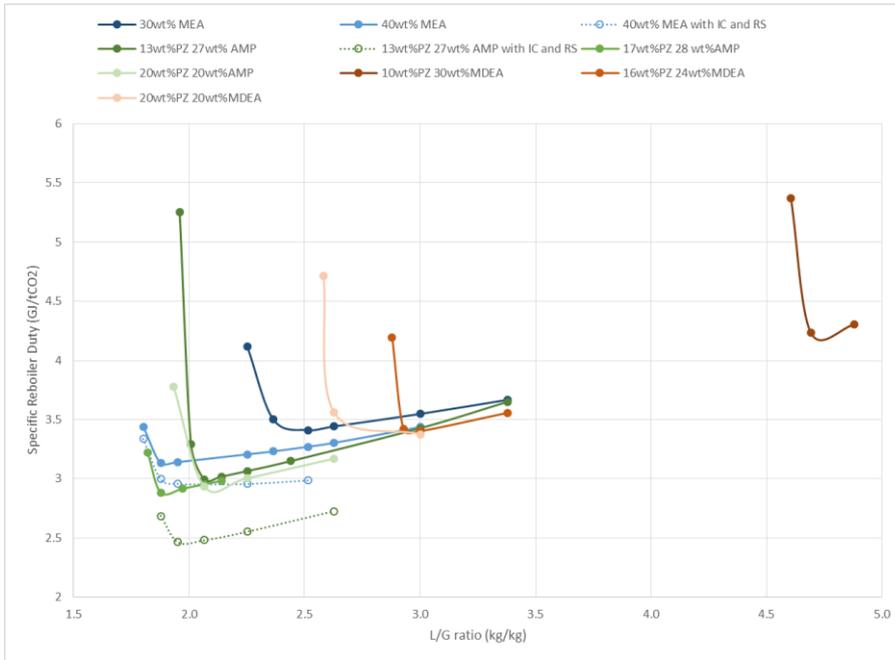


Figure 33 Energy required to capture 90% of the inlet CO₂ from ultra-supercritical pulverised coal flue gas for various liquid absorbents

AMP = amino-methyl-propanol; IC = inter cooling; MDEA = methyl-diethanolamine; MEA = monoethanolamine; PZ = piperazine; RS = rich split

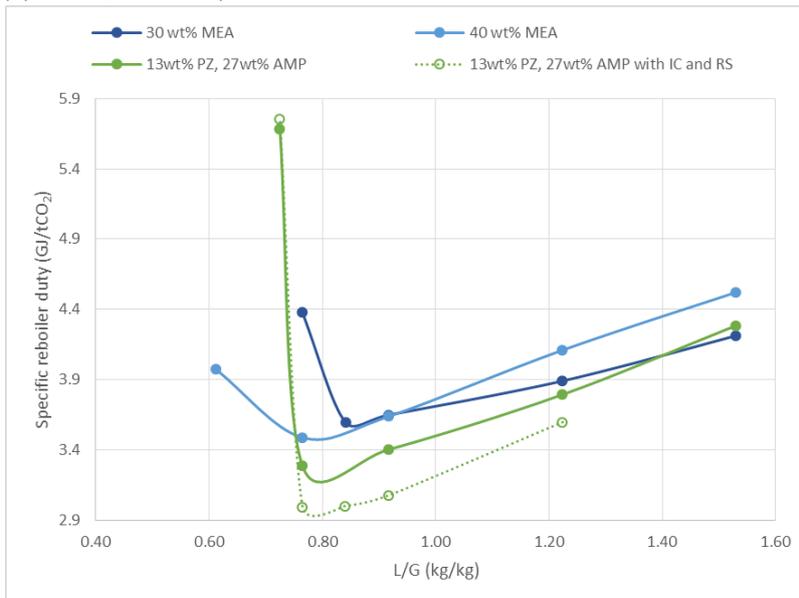


Figure 34 Energy required to capture 90% of the inlet CO₂ from natural gas combined-cycle flue gas for various liquid absorbents

AMP = amino-methyl-propanol; IC = inter cooling; MEA = monoethanolamine; RS = rich split

A comparison of the different amine formulations shows that for both the USCPC and the NGCC, a minimum reboiler duty was achieved for the (13 wt%) PZ/(27 wt%) AMP formulation. With the application of both intercooling and rich split, the specific reboiler duty was close that reported by technology suppliers for their proprietary systems, i.e. ~2.5 GJ/t CO₂ for USCPC and ~3.0 GJ/t CO₂ for NGCC. We therefore decided to use this PZ/AMP formulation as the new baseline absorption liquid, which is quite similar to the 4 m AMP/2 m PZ mixture

identified by Voice (2013) as a formulation that “minimizes amine oxidation while maintaining excellent rate and thermodynamic properties for CO₂ capture”.

In further simulations, 2 wt% formate was added to the amine formulation to represent a typical heat-stable salt content encountered in most operational amine plants. A 20°C temperature approach was used for the lean/rich cross heat exchanger at the cold end. This large temperature approach was used to reflect the performance of an in-service, fouled, heat exchanger. Further simulations resulted in the definition of the optimum column properties provided in Table 46, and use the process design as illustrated in Figure 35. The same plant layout was used for both the USCPC and NGCC flue gas simulations. This layout also included a wash section to simulate the effect of amine recovery from the exhaust gases.

Table 46 Column properties used in amine-based post-combustion capture simulations

PROPERTY	PRE-TREATMENT COOLER	ABSORBER	ABSORBER WASH	STRIPPER
Packed height, m	5	20	5	10 (2 m in rectifying section)
Packing type	Pall rings 90 mm	Mellapak M250X	Mellapak M250X	Mellapak M250X
Column diameter	80% flood	80% flood	80% flood	80% flood
Pressure at base of column, kPa-absolute	108	105	100	185

A point near the minimum energy operating point (as outlined in Figure 33 and Figure 34) at 90% CO₂ capture was selected as the plant’s operating point.

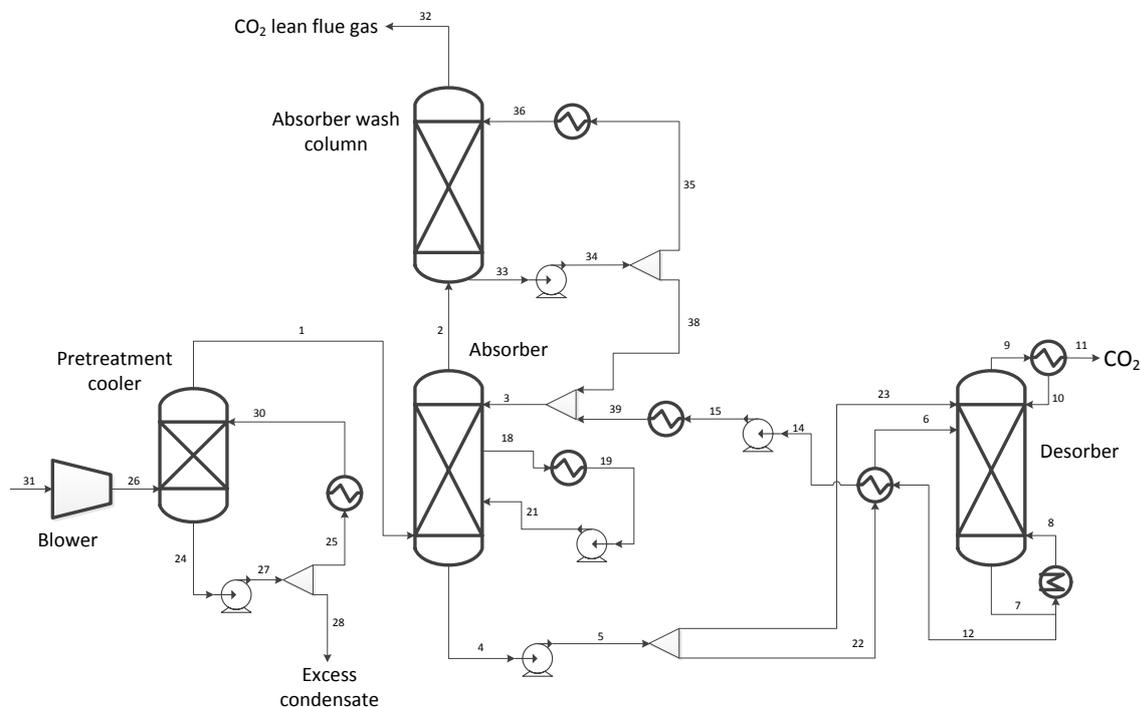


Figure 35 Line diagram of CO₂-capture plant used in amine-based post-combustion capture simulations; layout includes absorber intercooling and rich-split process modifications

Operational properties for the columns determined from the process simulations are shown in Table 47.

Table 47 Amine-based post-combustion capture simulation results related to column operation for ultra-supercritical pulverised coal (USCPC) and natural gas combined-cycle (NGCC) power plants

PARAMETER	USCPC	NGCC
Pre-treatment cooler diameter, m	11.0	12.0
Pre-treatment cooler pressure drop, kPa	1.8	1.9
Absorber diameter, m	10.7	10.6
Absorber pressure drop, kPa	3.1	4.3
Absorber wash diameter, m	9.9	10.6
Absorber wash pressure drop, kPa	0.9	1.1
Stripper diameter, m	5.6	3.9
Stripper pressure drop, kPa	0.8	0.6
Liquid/gas ratio, kg/kg	1.99	0.84
Position of intercooling, m	17	17
Fraction of rich absorbent flow split to top of column, %	33	17

The stream data for the points indicated in the line diagram in Figure 35 are provided in Table 48 for the USCPC case, and in Table 49 for the NGCC.

The CO₂ product was compressed to 110 bar in a four-stage process using the flow diagram presented in Figure 36. Intercooling was performed with the condensate from the steam turbine, where the temperature levels enabled this. After the first and second stage, additional cooling was used.

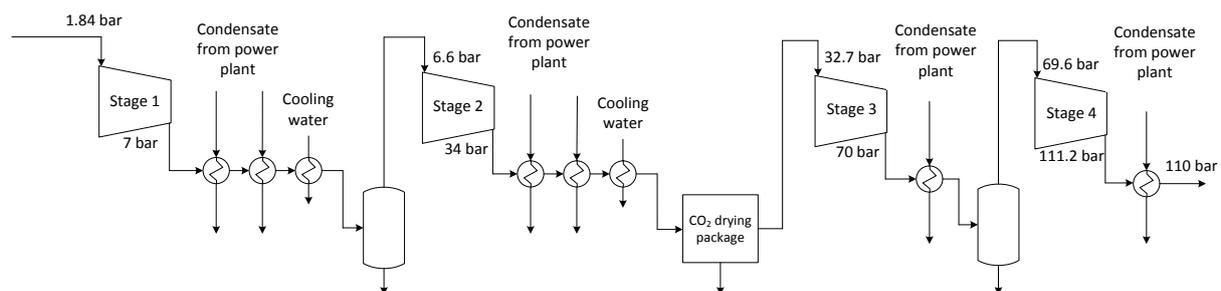


Figure 36 Four-stage CO₂-compression flow diagram

An overview of the performance of the PCC process is provided in Table 50. A comparison with the results in Table 44 indicates that the chosen amine system and process design can reproduce the specific reboiler duty and specific absorption liquid flow rate that vendors have reported. The electricity requirement is underestimated, also noting a large difference between the coal and gas cases for the chosen system. In the data reported by vendors, it is not clear if the electricity requirement for the cooling-water pumps is taken into account. The calculated amine concentrations after the wash section are higher than those reported by the

vendors. This reflects the fact that a simple wash section is not the optimum representation of the sophisticated emission-reduction systems that vendors have developed, which may incorporate a separate acid wash or systems that limit aerosol-induced emissions.

Table 48 Stream data for 90% capture from ultra-supercritical pulverised coal flue gas

Stream		1	2	3	4	5	6	7	8	9	10
Water	mol%	7.11	22.64	86.49	80.46	80.46	80.46	86.81	95.22	6.78	99.43
Carbon Dioxide	mol%	14.16	1.39	0.44	6.31	6.31	6.31	0.79	2.86	93.20	0.32
Piperazine	mol%	0.00	0.04	3.96	4.01	4.01	4.01	3.72	0.32	0.00	0.04
AMP	mol%	0.00	0.09	7.92	8.01	8.01	8.01	7.57	1.60	0.01	0.20
Nitrogen	mol%	74.40	71.67	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
Nitric Oxide, Argon	mol%	0.85	0.81	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Oxygen	mol%	3.49	3.36	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Formate (heat- stable salt, HSS)	mol%	0.00	0.00	1.19	1.21	1.21	1.21	1.11	0.00	0.00	0.00
Total flow	kmol/s	8.96	9.31	19.79	19.45	19.45	13.03	21.21	2.96	1.23	0.04
Total flow	kg/s	266.43	243.78	529.99	552.62	552.62	370.26	560.83	59.43	51.90	0.64
Temperature	°C	40.00	57.47	41.48	44.70	44.70	103.06	122.37	123.14	50.17	40.00
Pressure	kPa	106.19	101.90	105.00	105.00	185.00	185.00	185.00	185.00	184.18	184.18

Stream		11	12	13	14	15	16	17	18	19	20
Water	mol%	4.04	85.45	85.45	85.45	85.45	86.49	86.49	80.76	80.76	80.76
Carbon Dioxide	mol%	95.95	0.45	0.45	0.45	0.45	0.44	0.44	5.88	5.88	5.88
Piperazine	mol%	0.00	4.27	4.27	4.27	4.27	3.96	3.96	4.05	4.05	4.05
AMP	mol%	0.00	8.54	8.54	8.54	8.54	7.92	7.92	8.09	8.09	8.09
Nitrogen	mol%	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Nitric Oxide, Argon	mol%	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Oxygen	mol%	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Formate (heat- stable salt, HSS)	mol%	0.00	1.29	1.29	1.29	1.29	1.19	1.19	1.22	1.22	1.22
Total flow	kmol/s	1.19	18.26	18.26	18.26	18.26	19.79	19.79	19.27	19.27	19.27
Total flow	kg/s	51.26	501.40	501.40	501.43	501.43	530.01	529.99	547.07	547.07	547.07
Temperature	°C	40.00	123.14	123.14	64.70	64.70	41.48	41.48	45.27	40.00	40.00
Pressure	kPa	184.18	185.00	185.00	185.00	105.00	105.00	105.00	104.58	104.58	105.00

Stream		21	22	23	24	25	26	27	28	29	30
Water	mol%	80.76	80.46	80.46	99.99	99.99	12.10	99.99	99.99	99.99	99.99
Carbon Dioxide	mol%	5.88	6.31	6.31	0.01	0.01	13.40	0.01	0.01	0.01	0.01
Piperazine	mol%	4.05	4.01	4.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
AMP	mol%	8.09	8.01	8.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Nitrogen	mol%	0.00	0.00	0.00	0.00	0.00	70.40	0.00	0.00	0.00	0.00
Nitric Oxide, Argon	mol%	0.00	0.00	0.00	0.00	0.00	0.80	0.00	0.00	0.00	0.00
Oxygen	mol%	0.00	0.00	0.00	0.00	0.00	3.30	0.00	0.00	0.00	0.00
Formate (heat- stable salt, HSS)	mol%	1.22	1.21	1.21	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total flow	kmol/s	19.27	13.03	6.42	44.91	44.40	9.47	44.91	0.51	44.40	44.40
Total flow	kg/s	547.07	370.26	182.37	809.17	800.00	275.60	809.17	9.17	800.00	800.00
Temperature	°C	40.00	44.70	44.70	47.49	47.49	56.89	47.49	47.49	39.50	39.50
Pressure	kPa	105.00	185.00	185.00	108.00	110.00	108.00	110.00	110.00	110.00	110.00

Stream		31	32	33	34	35	36	37	38	39
Water	mol%	12.10	7.60	98.90	98.90	98.90	98.90	98.90	98.90	85.45
Carbon Dioxide	mol%	13.40	1.60	0.34	0.34	0.34	0.34	0.34	0.34	0.45
Piperazine	mol%	0.00	0.00	0.22	0.22	0.22	0.22	0.22	0.22	4.27
AMP	mol%	0.00	0.00	0.54	0.54	0.54	0.54	0.54	0.54	8.54
Nitrogen	mol%	70.40	85.81	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Nitric Oxide, Argon	mol%	0.80	0.98	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Oxygen	mol%	3.30	4.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Formate (heat- stable salt, HSS)	mol%	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.29
Total flow	kmol/s	9.47	7.77	31.04	31.04	29.51	29.51	29.51	1.53	18.26
Total flow	kg/s	275.60	215.20	578.59	578.59	550.00	550.00	550.00	28.59	501.43
Temperature	°C	50.00	35.56	63.19	63.19	63.19	32.20	32.20	63.19	40.00
Pressure	kPa	101.80	99.10	100.00	105.00	105.00	105.00	105.00	105.00	105.00

Table 49 Stream data for 90% capture from natural gas combined-cycle flue gas

Stream		1	2	3	4	5	6	7	8	9	10
Water	mol%	7.15	12.04	86.23	81.77	81.77	81.77	86.32	92.38	21.10	99.65
Carbon Dioxide	mol%	4.26	0.45	0.75	5.09	5.09	5.09	1.39	5.91	78.87	0.21
Piperazine	mol%	0.00	0.02	3.94	3.98	3.98	3.98	3.69	0.27	0.00	0.02
AMP	mol%	0.00	0.05	7.89	7.95	7.95	7.95	7.48	1.44	0.02	0.12
Nitrogen	mol%	75.50	74.52	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
Nitric Oxide, Argon	mol%	0.91	0.90	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Oxygen	mol%	12.18	12.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Formate (heat-stable salt, HSS)	mol%	0.00	0.00	1.19	1.21	1.21	1.21	1.11	0.00	0.00	0.00
Total flow	kmol/s	11.48	11.63	10.25	10.10	10.10	8.38	10.99	1.35	0.56	0.10
Total flow	kg/s	326.89	318.85	275.01	283.02	283.02	234.91	291.26	27.95	21.52	1.81
Temperature	°C	39.94	48.92	40.51	43.83	43.83	101.27	121.52	122.15	64.22	40.00
Pressure	kPa	106.09	100.74	105.00	105.00	185.00	185.00	185.00	185.00	184.38	184.38

Stream		11	12	13	14	15	16	17	18	19	20
Water	mol%	4.05	85.47	85.47	85.47	85.47	86.23	86.23	81.55	81.55	81.55
Carbon Dioxide	mol%	95.93	0.76	0.76	0.76	0.76	0.75	0.75	5.17	5.17	5.17
Piperazine	mol%	0.00	4.17	4.17	4.17	4.17	3.94	3.94	4.02	4.02	4.02
AMP	mol%	0.00	8.33	8.33	8.33	8.33	7.89	7.89	8.04	8.04	8.04
Nitrogen	mol%	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Nitric Oxide, Argon	mol%	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Oxygen	mol%	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Formate (heat-stable salt, HSS)	mol%	0.00	1.27	1.27	1.27	1.27	1.19	1.19	1.22	1.22	1.22
Total flow	kmol/s	0.46	9.64	9.64	9.64	9.64	10.25	10.25	10.00	10.00	10.00
Total flow	kg/s	19.71	263.31	263.31	263.31	263.31	274.98	275.01	281.48	281.48	281.48
Temperature	°C	40.00	122.15	122.15	63.83	63.83	40.51	40.51	42.08	40.00	40.00
Pressure	kPa	184.38	185.00	185.00	185.00	105.00	105.00	105.00	104.39	104.39	105.00

Stream		21	22	23	24	25	26	27	28	29	30
Water	mol%	81.55	81.77	81.77	100.00	100.00	8.50	100.00	100.00	100.00	100.00
Carbon Dioxide	mol%	5.17	5.09	5.09	0.00	0.00	4.20	0.00	0.00	0.00	0.00
Piperazine	mol%	4.02	3.98	3.98	0.00	0.00	0.00	0.00	0.00	0.00	0.00
AMP	mol%	8.04	7.95	7.95	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Nitrogen	mol%	0.00	0.00	0.00	0.00	0.00	74.40	0.00	0.00	0.00	0.00
Nitric Oxide, Argon	mol%	0.00	0.00	0.00	0.00	0.00	0.90	0.00	0.00	0.00	0.00
Oxygen	mol%	0.00	0.00	0.00	0.00	0.00	12.00	0.00	0.00	0.00	0.00
Formate (heat-stable salt, HSS)	mol%	1.22	1.21	1.21	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total flow	kmol/s	10.00	8.38	1.72	44.58	44.41	11.65	44.58	0.17	44.41	44.41
Total flow	kg/s	281.48	234.91	48.11	803.05	800.00	329.94	803.05	3.05	800.00	800.00
Temperature	°C	40.00	43.83	43.83	46.74	46.74	93.05	46.74	46.74	39.00	39.00
Pressure	kPa	105.00	185.00	185.00	108.00	110.00	108.00	110.00	110.00	110.00	110.00

Stream		31	32	33	34	35	36	37	38	39
Water	mol%	8.50	7.27	98.11	98.11	98.11	98.11	98.11	98.11	85.47
Carbon Dioxide	mol%	4.20	0.44	0.51	0.51	0.51	0.51	0.51	0.51	0.76
Piperazine	mol%	0.00	0.00	0.42	0.42	0.42	0.42	0.42	0.42	4.17
AMP	mol%	0.00	0.00	0.96	0.96	0.96	0.96	0.96	0.96	8.33
Nitrogen	mol%	74.40	78.65	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Nitric Oxide, Argon	mol%	0.90	0.95	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Oxygen	mol%	12.00	12.68	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Formate (heat-stable salt, HSS)	mol%	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.27
Total flow	kmol/s	11.65	11.02	21.54	21.54	20.93	20.93	20.93	0.61	9.64
Total flow	kg/s	329.94	307.18	411.67	411.67	400.00	400.00	400.00	11.67	263.31
Temperature	°C	85.20	35.87	50.07	50.07	50.07	31.20	31.20	50.07	40.00
Pressure	kPa	101.80	98.89	100.00	105.00	105.00	105.00	105.00	105.00	105.00

Table 50 Overview of performance parameters for the post-combustion capture process in ultra-supercritical pulverised coal (USPC) and natural gas combined-cycle (NGCC) power stations

PARAMETER	USPC	NGCC
Reboiler duty	2.46 GJ/t CO ₂	3.00 GJ/t CO ₂
Absorption flow (based on lean solution flow rate)	10.4 m ³ /t CO ₂	13.5 m ³ /t CO ₂
Electricity for PCC (pumps, blower but not cooling water)	15.9 kWh/t CO ₂	47.0 kWh/t CO ₂
Cooling requirement for PCC	3.01 GJ/t CO ₂	4.40 GJ/t CO ₂
Compression	105 kWh/t CO ₂	
Amine content in exhaust	PZ : 0.5 ppm AMP : 5.5 ppm	PZ : 1.4 ppm AMP : 12.1 ppm

8.6 Techno-economic results for power plants integrated with PCC

We carried out the economic performance assessment using 2015 as the most recent year that data for the capture plant cost were available in the Aspen Plus cost estimator. The results are summarised in Table 51.

Table 51 Overview of techno-economic analysis for power plants without post-combustion capture (W/O PCC), and with standard monoethanolamine (MEA) or piperazine/amino-methyl-propanol (PZ/AMP) liquid absorbent

	Ultra-supercritical coal-fired power plant			Natural gas combined cycle power plant		
	W/O PCC	MEA	PZ/AMP	W/O PCC	MEA	PZ/AMP
Technical performance						
Gross power output (MW)	900	900	900	890	890	890
Auxiliary power (MW)	83	266.1	215.6	12	161.8	128.2
Net power output (MW)	817	633.9	684.4	878	728.2	761.9
Net plant HHV efficiency (%)	42.5	32.97	35.59	52.66	43.91	45.94
Net plant LHV efficiency (%)	44.4	34.48	37.23	58.25	48.57	50.82
CO ₂ generation (t/h)	604	604	603.3	310	310	310
CO ₂ emission (t/h)	604	61	59.1	310	31	31
CO ₂ emission (t/MWh)*	0.739	0.095	0.084	0.353	0.042	0.040
CO ₂ capture (t/h)	0	543	544	0	279	279
Equivalent energy consumption (MWh/t CO ₂)	–	0.337	0.244	–	0.506	0.423
Economic performance						
Total capital requirement (million €)	1342.8	1681.1	1659.5	835.7	1172.8	1166.3
Specific capital requirement (€/kW)	1647	2654	2424	939	1611	1531
Fixed O&M (million €)	37.7	46.3	45.9	29.2	39.7	39.5
Variable O&M (million €)	7.54	20.1	17.8	3.41	11.9	9.1

	Ultra-supercritical coal-fired power plant			Natural gas combined cycle power plant		
	W/O PCC	MEA	PZ/AMP	W/O PCC	MEA	PZ/AMP
LCOE (€/MWh)	51.6	87.0	79.5	52.9	77.6	73.8
CO ₂ -avoided cost (€/t CO ₂)	–	55.0	42.8	–	79.3	67.1

Note: CO₂ emissions include CO₂ contained in the combustion air. The LCOE values in Table 49 follow those calculated in IEAGHG 2019-02, and use different fuel and T&S costs compared to those calculated in Part I of this report.

The use of PZ/AMP instead of MEA significantly improved generation efficiency for both power plants. The USCPC efficiency reduction at 90% CO₂ capture decreased from 9.9 percentage points to 7.2 percentage points based on LHV, reflecting a 27% improvement in energy consumption for capture and compression. In the NGCC, the efficiency reduction at 90% CO₂ capture decreased from 9.7% percentage points to 7.4 percentage points based on LHV, reflecting a 16% improvement in the energy consumption for capture and compression.

The use of PZ/AMP instead of MEA resulted in the increase in LCOE at 90% CO₂ capture from the USCPC being reduced from a 69% increase to a 54% increase. This is equivalent to a 21% cost reduction, similar to the reduction in the CO₂-avoided cost. For the NGCC, the use of PZ/AMP instead of MEA resulted in the increase in levelised cost of electricity (LCOE) at 90% CO₂ capture being reduced from a 47% increase to 40%. This is equivalent to a 15% cost reduction, similar to the reduction in the CO₂-avoided cost.

The new PZ/AMP-based PCC technology has only a small effect on the total capital requirement for both power stations, i.e. –1.3% for the USCPC and –0.6% for the NGCC, compared with MEA. This indicates that the main benefits are derived from the improved energy performance of the new PCC system and its integration into the power plant.

The detailed techno-economic results are given in Appendix D.

9 Conclusions

For many years, a solution of 30 wt% MEA has been used as the benchmark PCC technology against which new and improved technologies are compared. Today, two commercial-scale demonstrations of amine-based technologies (Boundary Dam project and PetraNova project) are applied to coal power-station flue gas streams, but neither project employ this baseline absorbent. Amine-based liquid-absorbent CO₂ capture technology has seen significant development in the past 5–10 years, with current commercially available technologies all suggesting significantly better techno-economic performances than the baseline MEA process. Thus, the benchmark technology must be updated to ensure that any potential benefit arising from future technology developments are visible against the current commercial offerings.

The new benchmark should reflect the performances achieved with current state-of-the-art PCC technologies. To this end, we assessed the technical performance characteristics of commercially available technologies as available in the public domain. We hypothesised that the current process performances, as reported by the technology suppliers, could be reproduced through amine process modelling with suitable formulations. For this purpose, an ultra-supercritical coal-fired power station and a natural-gas-fired combined-cycle power station were modelled in EBSILON® in accordance with the IEAGHG technical and economical assessment criteria as previously defined. This generated the flue gas streams for which the PCC options with alternative amine formulations were explored.

While a large number of formulations are possible, our analysis focused on those amines for which ample information was available in the public domain, and for which process modelling could be carried out using standard gas-treatment software. We used ProTreat® to simulate the CO₂-capture process in this study, investigating solutions of concentrated MEA, and mixtures of PZ with MDEA and AMP. A 40 wt% formulation of PZ/AMP in a 1:2 molar ratio was selected as representative of the current state of the art.

A PCC process configuration with absorber intercooling and rich-split flow was selected to reflect the fact that the technology suppliers use a variety of process designs to optimise the process performance. The specific reboiler duties determined reflected those reported by the suite of technology suppliers. Finally, we performed a techno-economic evaluation of the PCC process, which indicated that the costs of capture with respect to 30% MEA for the coal-fired power station were reduced by 22%, and for the natural-gas-fired combined cycle by 15%.

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Appendix B Selected commercially available, amine-based, post-combustion CO₂-capture technologies

B.1 Mitsubishi Heavy Industries

Mitsubishi Heavy Industries (MHI) have been developing post-combustion capture (PCC) technologies since 1990 (Suda et al. 1992). Their proprietary KS1 absorption liquid is based on sterically hindered amines and was developed in collaboration with the Kansai Electric Power Company (Mimura et al. 1995; Mimura et al. 1997). It is reported to have the following beneficial properties with respect to a 30% monoethanolamine (MEA) solution (Imai 2003):

- lower heat of absorption at 70–75 kJ/mol CO₂
- higher cyclic loading resulting in a 40% reduction in the absorption liquid flow rate
- ten-fold reduction in amine consumption as shown through decreased build-up of heat-stable salts and reduced degradation
- approximate 25-fold reduction in corrosion compared with uninhibited MEA and 2 to 3-fold reduction compared with inhibited MEA.

The MHI technology also includes an energy-saving process design that uses the heat available in the lean absorption liquid from the stripper and the reboiler condensate for the liquid-regeneration process. This results in a 15% reduction in the thermal energy requirement compared with the conventional process design.

MHI was the first to report on the issue of aerosol-induced emissions of amines in coal-fired power stations and pioneered technical solutions for this (Kamijo 2011).

MHI has deployed their KM-CDR[®] process in 12 plants commercially, with a total capacity of 4550 t/d CO₂ in various CO₂-reuse applications (methanol, urea) (Kamijo 2015; Miyamoto et al. 2017). These operate mostly on flue gases from natural gas combustion and gases from reformers. The technology was also demonstrated on a coal-fired power plant in Alabama (Plant Barry, Southern Company) between 2011 and 2014 at a 500 t/day CO₂ scale, and at a smaller scale in a facility in Brindisi, Italy, owned by ENEL (Kamijo et al. 2013).

This was followed by the successful start of the Petra Nova project in 2017, in which the KM-CDR[®] process is used to capture 4776 t/d CO₂ from a coal-fired power plant owned by NRG (W.A. Parish Power unit 8) in Texas. The commercial-scale facility provides CO₂ for enhanced oil recovery in the West Ranch oil Field. The PCC process flow sheet in the Petra Nova project is shown in Figure B.1. An overview of the performance of the MHI absorbent is provided in Table B.1.

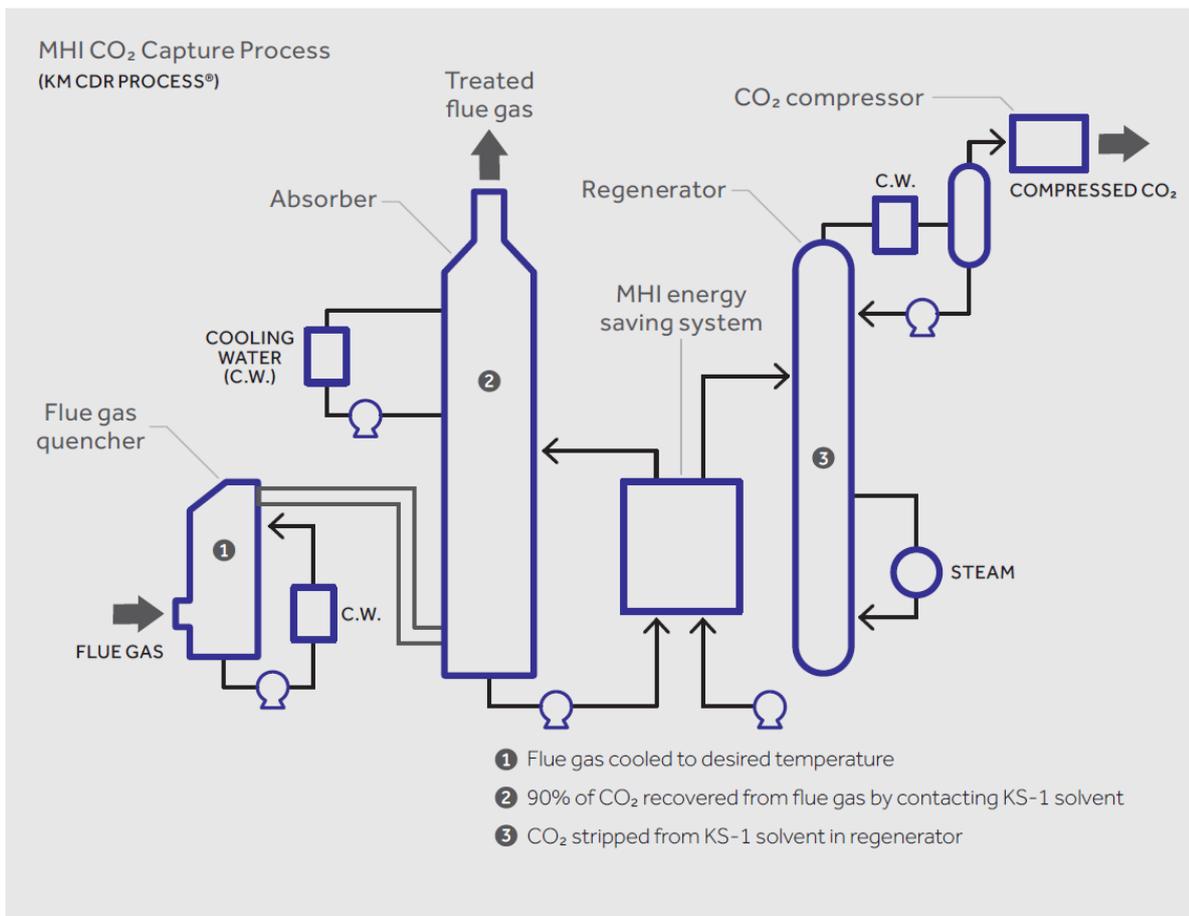


Figure B.1 Post-combustion CO₂ capture process flow sheet for the Petra Nova project (NRG Factsheet Carbon Capture: Petra Nova CO₂ capture project, Thompsons, TX)

Table B.1 Performance overview of MHI absorbent

PARAMETER	VALUE	SOURCE
Reboiler duty (90% capture coal-fired power plant)	2.6 GJ/tonne CO ₂	Yagi et al. 2004
Electrical-energy requirement	77 kWh/tonne CO ₂ (coal-fired power plant)	Ibid.
Ammonia emission	0.3–2.0 ppm (18 ppm for 30% MEA in same pilot plant)	Kamijo et al. 2013
Absorption liquid flow	10 m ³ /tonne CO ₂ (~13 m ³ /tonne CO ₂ for 30% MEA in same pilot plant)	Ibid.
Amine emission	0.7–3 ppm (12–35 ppm before introduction of proprietary emission-reduction system)	Kamijo 2014
Cooling-water requirement	150 m ³ /tonne CO ₂ (based on ΔT = 10 K)	Yagi et al. 2004
Amine consumption	0.35 kg/tonne CO ₂	Ibid.

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B.2 Shell Cansolv

Cansolv has pioneered the use of amine solutions for SO₂ removal in exhaust gases from fluid catalytic crackers, smelters and power plants, with the first commercial plants dating back to 2002 (Ryan 2009). Using their combined experience of handling of flue gases and amine solutions, Cansolv also developed an amine-based PCC processes. The technology has been trialled at pilot-plant scale in diverse CO₂-capture applications, such as in the pulp and paper industry, cement industry, blast furnaces and the power sector. Shell acquired Cansolv in 2008.

The Shell Cansolv process was deployed in the SaskPower Integrated Carbon Capture and Storage Demonstration Project at the Boundary Dam power plant in Saskatchewan, Canada (IEAGHG 2015). This project, started up in 2014, was the first large-scale demonstration of amine-based PCC technology. The process design integrates the capture of SO₂ and CO₂ to provide optimum performance. This configuration results in useful sulfuric acid by-product.

Figure B.2 provides a typical process flow diagram that incorporates absorber intercooling and lean amine vapour recompression for optimum energy performance. Shell Cansolv has developed a range of absorption liquids, such as DC103 and DC201. The use of lean amine vapour compression is less advantageous with an improved absorption liquid such as DC201 (Abdollahi et al. 2015).

An overview of the performance of the Shell Cansolv process is provided in Table B.2.

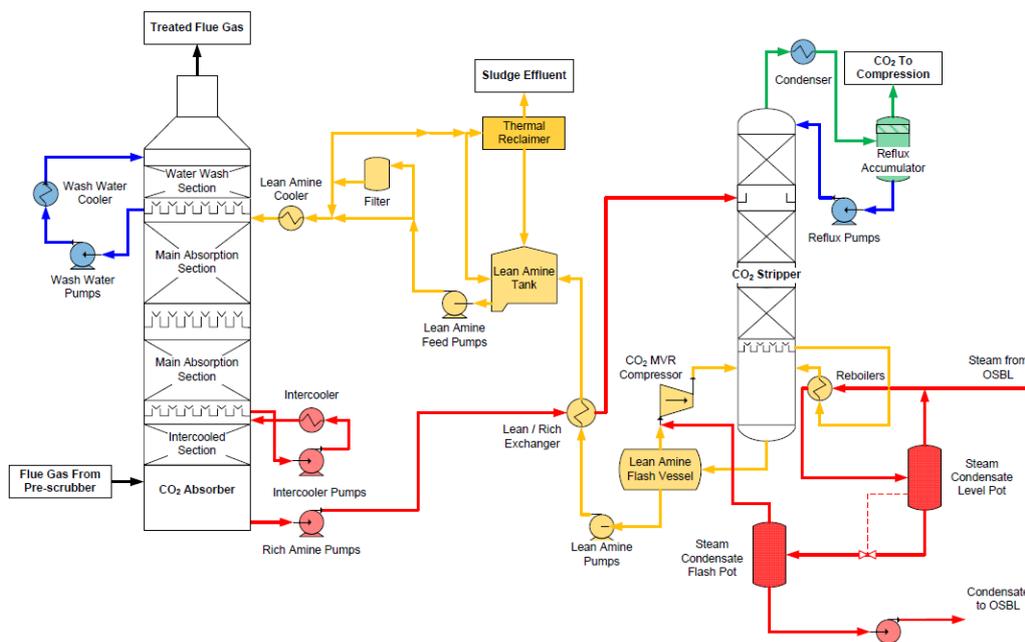


Figure B.2 Typical flow diagram of Shell Cansolv PCC process (Singh and Stéphenne, 2014)

Table B.2 Performance overview of Shell Cansolv process

PARAMETER	VALUE	SOURCE
Reboiler duty (90% capture coal-fired power plant)	DC-103: 2.3 GJ/tonne CO ₂ (with vapour recompression)	Singh et al. 2014
	DC-201: 2.2–2.8 GJ/tonne CO ₂	Just 2013

Reboiler duty (90% capture gas-fired combined-cycle)	2.9 GJ/tonne CO ₂	Derived from Peterhead carbon capture and storage (CCS) project 2016
	DC-103: 2.9 GJ/tonne CO ₂ DC-201: 2.3 GJ/tonne CO ₂	Design performances mentioned National Carbon Capture Center 2014
Electrical-energy requirement (coal-fired power plant)	DC-103: 70 kWh/tonne CO ₂	Ryan 2009
Electrical-energy requirement (gas-fired combined-cycle)	200 kWh/tonne CO ₂ (including 100 kWh/tonne CO ₂ for compression)	Derived from Peterhead CCS project 2016
Absorption liquid flow	11 m ³ /tonne CO ₂	Derived from Peterhead CCS project 2016
	DC-103: 16 m ³ /tonne CO ₂ DC-201: 10 m ³ /tonne CO ₂	Design performances mentioned National Carbon Capture Center 2014
Cooling-water requirement	Total: 200 m ³ /tonne CO ₂ (based on ΔT=10K; closed loop, flue gas and water wash cooling) Capture: 64 m ³ /tonne CO ₂ (based on ΔT=10K; excluding flue gas and water wash cooling)	Derived from Peterhead CCS project 2016
	DC-103: 44 m ³ /tonne CO ₂ DC-201: 23 m ³ /tonne CO ₂	Design performances mentioned National Carbon Capture Center 2014
Amine consumption	DC-103: 0.1 kg/tonne CO ₂ (expected)	Ryan 2009
Amine/ammonia emission	No data found	–

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B.3 Fluor

The Econamine FG CO₂ recovery process was acquired by Fluor Inc. from the Dow Chemical Company in 1989. The technology uses aqueous solutions of monoethanolamine (MEA) with a proprietary corrosion inhibitor (Sander et al. 1992). Fluor has continuously improved this process, resulting in the Econamine FG PlusSM technology, which currently includes the following improvements (Scherffius et al. 2013; Reddy et al. 2008):

- a flue gas conditioning system designed to cool the flue gas and reduce the SO₂ concentration
- absorber intercooling
- lean vapour compression in the liquid-regeneration system
- advanced absorption liquid formulation
- advanced solvent-reclaiming technology

These improvements aim to reduce energy consumption, capital cost and amine loss, and improve the environmental signature.

Fluor has ample commercial plant experience removing CO₂ from dilute sources. Twenty-seven units have been licensed so far. Econamine FG Plus is the only technology in the world that has been commercially proven in CO₂ recovery from gas-turbine exhausts. This experience was gained with a natural-gas-fired combined-cycle in Bellingham, Massachusetts. The Econamine FGSM plant was designed and constructed by Fluor and was maintained in continuous operation from 1991 to 2005. Fluor has also obtained significant practical experience with flue gases from coal-fired power plants through operation of a 70 t/d PCC pilot plant in a collaboration with EON (now Uniper) at a power station in Wilhelmshaven, Germany (Radgen et al. 2014).

Large-scale CO₂ sequestration projects require multiple CO₂ absorption trains, resulting in large plot areas. Smaller CO₂-capture retrofit applications may find plot availability plays a vital role in the feasibility of the project. Fluor has focused on strategies to minimise the footprints of Econamine FG Plus plants. For large-scale CO₂ capture applications, Fluor has developed absorbers designs with diameters of up to 60 feet, to minimise the number of absorption trains. Fluor has experience with the design and construction of columns with diameters of 40 to 50 feet.

Figure B.3 provides a process flow diagram for Fluor's Econamine FG Plus process. An overview of the performance of the Econamine process is provided in Table B.3.

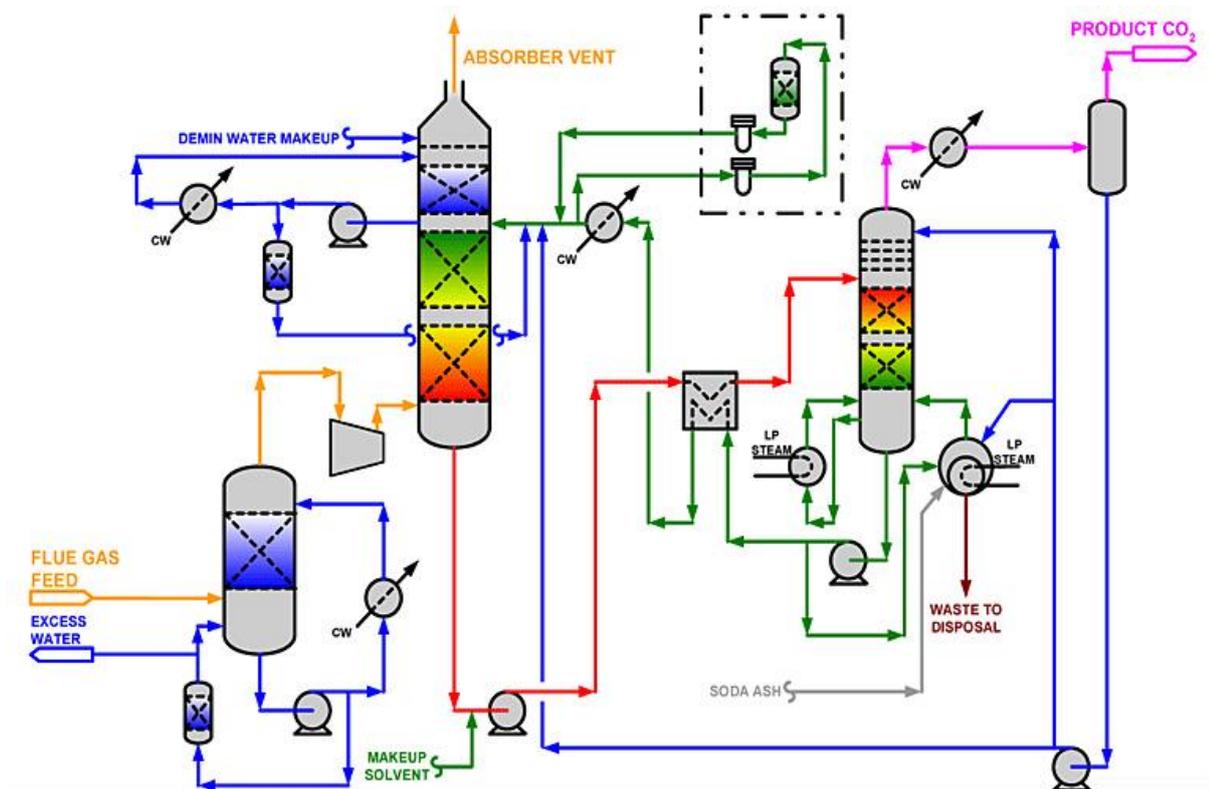


Figure B.3 Process flow diagram for Fluor's Econamine FG Plus process (Reddy and Gilmartin 2008)

Table B.3 Performance overview for Fluor Econamine

PARAMETER	VALUE	SOURCE
Reboiler duty (90% capture coal-fired power plant)	3.2 GJ/tonne CO ₂ (without vapour recompression)	IEAGHG 2004
Reboiler duty (90% capture gas-fired combined-cycle)	3.6 GJ/tonne CO ₂ (without vapour recompression)	IEAGHG 2004
Electrical-energy requirement (coal-fired power plant)	38 kWh/tonne CO ₂	Derived from NETL 2013
	~40 kWh/tonne CO ₂	Derived from Chapel et al. 1999
Electrical-energy requirement (gas-fired combined-cycle)	53 kWh/tonne CO ₂	Derived from NETL 2013
	~125 kWh/tonne CO ₂	Derived from Chapel et al. 1999
Absorption liquid flow	17 m ³ /tonne CO ₂	Derived from Chapel et al. 1999
Cooling-water requirement	196 m ³ /tonne CO ₂ (based on ΔT=8K)	Fluor/Statoil 2005
	82 m ³ /tonne CO ₂ (estimated; based on ΔT=10K)	Huizeling et al. 2011
Amine consumption	1.6 kg/tonne CO ₂ (expected)	Derived from Chapel et al. 1999
Amine emission	0.3 mg/Nm ³ (dry) (0.1 ppm)	Reddy et al. 2017
	2 mg/Nm ³ (full load) (0.7 ppm)	Huizeling et al. 2011
	1 ppm (both coal and gas)	IEAGHG 2004

PARAMETER	VALUE	SOURCE
	1 ppm (natural-gas-fired combined-cycle and residual catalytic cracker)	Fluor/Statoil 2005
Ammonia emission	1.7 mg/Nm ³ (dry) (2.2 ppm)	Reddy et al. 2017
	1 mg/Nm ³ (full load) (1.3 ppm)	Huizeling et al. 2011
	24 ppm (natural-gas-fired combined-cycle and residual catalytic cracker)	Fluor/Statoil 2005

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B.4 Aker Solutions

In partnership with The Norwegian University of Science and Technology (NTNU) and SINTEF, Aker Solutions have been developing PCC technology in the SOLVit project that operated between 2008 and 2015 (Knudsen et al. 2017). Pilot-plant research has been carried out at NTNU and SINTEF's Tiller facility using simulated flue gases and with Aker Solutions' Mobile Test Unit, and with EnBW's PCC pilot plant at Heilbronn in Germany using real flue gases. Aker Solutions has also evaluated their technology with the large amine plant at Technology Centre Mongstad (TCM) in Norway. In fact, Aker Solutions carried out the design, delivery and operation of the amine plant at TCM.

Apart from new amine formulations and an energy-saving process design, the Aker Solutions PCC technology also includes a thermal reclaimer and a proprietary emission control system that uses an acid wash and anti-mist system to limit emissions to the atmosphere.

An overview of the performance of the Aker Solutions PCC technology is provided in Table B.4.

Table B.4 Performance of Aker Solutions post-combustion capture technology

PARAMETER	VALUE	SOURCE
Reboiler duty (flue gas with 9% CO ₂)	2.8 GJ/tonne CO ₂	Gorset et al. 2014
Reboiler duty (87% capture gas-fired combined-cycle)	~3.4 GJ/tonne CO ₂ (for S21 and S26 – conventional process)	Ibid.
Absorption liquid flow	11.4–14.2 m ³ /tonne CO ₂	Derived from Southern Company 2014
Amine consumption	S21: 0.5–0.6 kg/tonne CO ₂ S26: 0.2–0.3 kg/tonne CO ₂ S26 in cement application: 0.15 kg/tonne CO ₂	Knudsen et al. 2017
Amine emission	0.6 mg/Nm ³ (0.1 ppm assuming MW = 100) 0.09 mg/Nm ³ (0.02 ppm assuming MW = 100) with acid wash	Knudsen et al. 2017
Ammonia emission	5 mg/Nm ³ (6.6 ppm) 0.01 mg/Nm ³ (0.1 ppm) with acid wash	Knudsen et al. 2017

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B.5 BASF-Linde

BASF and Linde have collaborated since 2009 to develop PCC technology together with power company RWE at their Niederaussem lignite-fired power station in Germany (Moser et al. 2013). BASF is marketing its entire gas-treating portfolio under the trade name OASE®, where OASE® blue is the brand for flue gas CO₂ capture. BASF systematically developed a new chemical absorption technology targeting the specific requirements of large-scale carbon-capture applications. Having screened more than 400 substances, about 20 component mixtures were then subjected to a proof-of-concept run in BASF’s mini plant where the complete CO₂ capture process was verified.

This valuable tool showed early on in the development whether or not a chemical solvent had the potential for further testing at pilot scale using real power plant off-gases containing CO₂. At the PCC pilot plant facility in Niederaussem, the amine-based technology was further demonstrated and optimised in several experimental campaigns lasting a total of 26,000 hours (Krishnamurthy et al. 2016).

The technology was also evaluated at the National Carbon Capture Center in Alabama for a period of 4109 hours, which involved parametric studies and a duration campaign. This validated the performance benefits of several unique equipment features incorporated in the pilot-plant design, such as a high-capacity structured packing, a gravity-driven absorber inter-stage cooler, the flue gas blower positioned downstream of the absorber, and a unique reboiler configuration that minimises solvent inventory and promotes a fast response to energy input requirements.

BASF also uses its proprietary dry-bed absorber configuration to reduce aerosol-induced emissions, and can employ a maximum pressure of 3.4 bar in the desorber as a result of the high thermal stability of the OASE® blue absorption liquids. An overview of the performance of OASE® blue is provided in Table B.5.

Table B.5 Performance of OASE® blue

PARAMETER	VALUE	SOURCE
Reboiler duty (90% capture, coal-fired power plant)	2.8 GJ/tonne CO ₂	Moser et al. 2013
	2.7 GJ/tonne CO ₂ (experimental)	Bostick 2017
	2.1–2.61 GJ/tonne CO ₂ (process simulations using different process designs)	
Electrical-energy requirement (coal-fired power plant)	22 kWh/tonne CO ₂	Derived from Bostick 2017
Amine consumption	0.3 kg/tonne CO ₂	Moser et al. 2013
Amine emission	1.5–2.3 mg/Nm ³ (estimated) (0.3–0.5 ppm assuming MW = 100)	Derived from Bostick 2017

Literature for BASF-Linde

Bostick, D., 2017, Slipstream pilot-scale demonstration of a novel amine-based post combustion technology for carbon dioxide capture from coal-fired power plant flue gas, Final testing report to National Carbon Capture Center, January 27, 2017.

- Krishnamurthy, K.R., Stoffregen, T., Rigby, S., O'Brien, K., 2016, Development and scale-up of an advanced aqueous amine-based post-combustion CO₂ capture utilizing BASF's OASE® blue technology, Presentation at CCUS conference, Tysons, Virginia, USA, June 14-16, 2016.
- Moser, P., Schmidt, S., Wallus, S., Ginsberg, T., Sieder, G., Clausen, I., Garcia-Palacois, J., Stoffregen, T., Mihailowitsch, D., 2013, Enhancement and long-term testing of optimised post-combustion capture technology – Results of the second phase of the testing programme at the Niederaussem pilot plant, Energy Procedia 37, 2377–2388.

B.6 Toshiba

Toshiba has been focusing on developing post-combustion capture technology since 2005. In 2009, they established a 10 t/d pilot plant at the Mikawa coal-fired thermal power plant in Fukuoka prefecture, Japan (Toshiba 2015). The plant is owned by Sigma Power Ariake Co. Ltd., a subsidiary of Toshiba. The laboratory research has focused on development of new amines and new amine formulations, progressively reducing both reboiler duty and amine degradation.

The new amines have been evaluated in the Mikawa facility with typical duration times being less than 1000 hours. A much larger facility (500 t/d) is being installed as part of the Japanese Ministry of Environment CCS project, in which the effect of amine emissions is being further investigated as part of the larger program on the environmental impact of CCS. The Mikawa Power Plant will be retrofitted to accommodate both coal and biomass-fired power generation. When the demonstration facility is completed in 2020, it will become the world's first power plant equipped with a large-scale carbon capture demonstration facility that is capable of capturing CO₂ from a biomass power plant.

Figure B.4 provides a process flow sheet of the PCC facility at Mikawa thermal power plant. An overview of the performance of the Toshiba absorbent achieved at the Mikawa plant is provided in Table B.6.

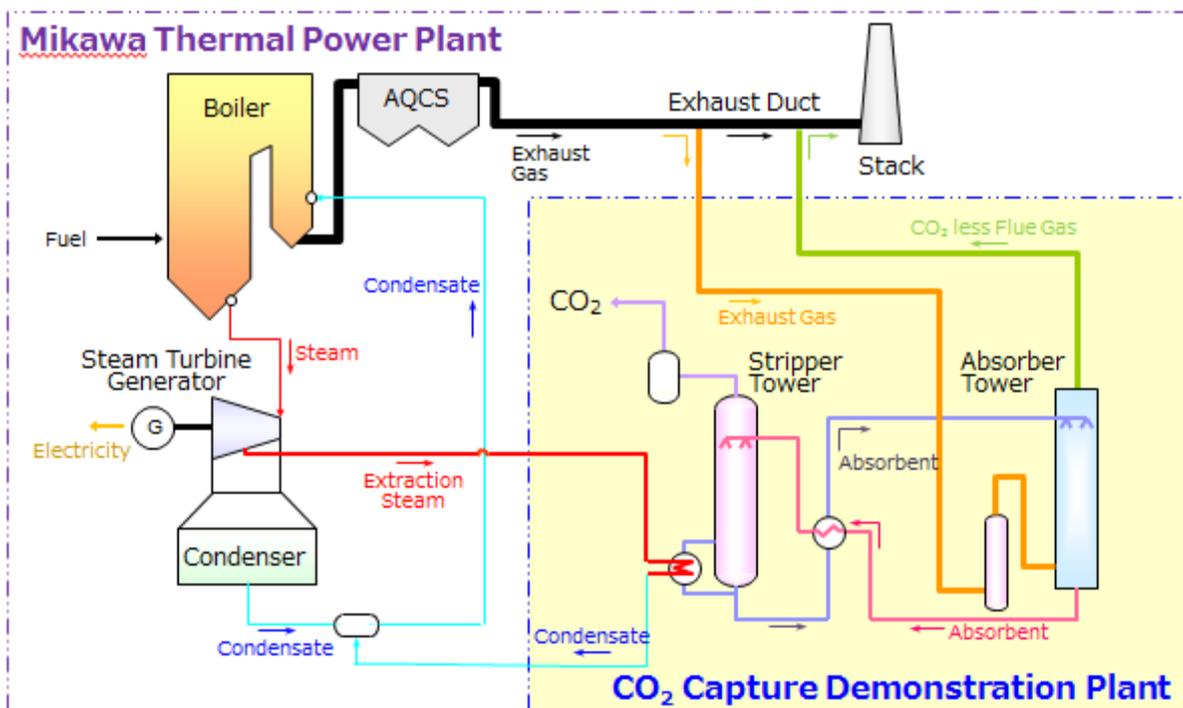


Figure B.4 Process flow sheet of post-combustion CO₂-capture facility at Mikawa thermal power plant (Suzuki, 2018)

Table B.6 Performance of Toshiba absorbent at the Mikawa thermal power plant

PARAMETER	VALUE	SOURCE
Reboiler duty (90% capture, coal-fired power plant)	2.6 GJ/tonne CO ₂ for TS-1	Saito et al. 2014
	2.35–2.4 GJ/tonne CO ₂ for newly developed amine formulations	
	3.0 GJ/tonne CO ₂	Saito et al. 2015
Absorption liquid flow	~17 m ³ /tonne CO ₂ (estimated, dependent on amine formulation used)	Saito et al. 2014

Literature for Toshiba

Saito, S., Udatsu, M., Kitamura, H., Murai, S., 2015, Mikawa CO₂-capture pilot plant test of new amine solvent, Presented at PCCC3, Regina, September 2015.

Saito, S., Udatsu, M., Kitamura, H., Murai, S., Kato, Y., Maezawa, Y., Watando, H., 2014, Development and evaluation of a new amine solvent at the Mikawa CO₂ capture pilot plant, Energy Procedia 51, 176–183.

Suzuki, K., Toshiba’s CO₂ Capture at Mikawa Thermal Power Plant, Japan CCS forum, June 18, 2018

Toshiba International Corp Pty Ltd/Toshiba Corporation in collaboration with Tongfang Environment Co. Ltd, August 2015, Applying carbon capture and storage to a Chinese steel plant, Report prepared for Global Carbon Capture and Storage Institute Ltd.

B.7 Hitachi

Hitachi has developed the H3 amine solution, which is suitable for use with flue gas from coal-fired boilers. Initially in joint research with The Tokyo Electric Power Company in the 1990s, the technology was trialled in a pilot plant capable of treating 1,000 m³ N/h of flue gas installed at the company's Yokosuka Power Plant. Since then, trials have also been conducted in the US with facilities at the Energy and Environmental Research Centre and the National Carbon Capture Center. The reboiler duty of the solution is 30% lower than that of MEA, and through the use of additives, the degradation rate was 70% less than that of MEA.

Key attributes of the H3-1 solvent are:

- low regeneration-energy demand, resulting in low steam consumption
- high net cycle carbon-absorption capacity, resulting in low solvent-circulation flow
- low solvent degradation and low amine loss, resulting in longer service life
- low corrosivity.

An overview of the performance of Hitachi's H3 amine solution is provided in Table B.7.

Table B.7 Performance of Hitachi's H3 amine solution

PARAMETER	VALUE	SOURCE
Reboiler duty (90% capture, coal-fired power plant)	2.4 GJ/tonne CO ₂	Babcock Hitachi, 2012

Literature for Hitachi

Babcock Hitachi, 2012, Testing of Hitachi H3-1 solvent at the National Carbon Capture Center: Final Report, Prepared by: National Carbon Capture Center, Hitachi Power Systems America, Ltd.

Honoki, M., Yokoyama, K., Takamoto, S., Kikkawa, H., Katsube, T., Kawasaki, T., Wu, S., Pavlish, B., Morton, F., 2013, Hitachi's carbon dioxide scrubbing technology with H3-1 absorbent for coal-fired power plants, *Energy Procedia* 37, 2188–2195.

Kawasaki, T., Inatsune, Y., Sano, K., Mishima, N., Miyake, Y., Kikkawa, H., Kiyama, K., Katube, T., Kuramoto, M., 2013, Demonstration of Hitachi's CO₂ capture system for flue gas from power plants, *Energy Procedia* 37, 1797–1803.

Appendix C Description of power plants

C.1 Ultra-supercritical coal-fired power plant

The performance of an ultra-supercritical coal-fired power plant was determined using EBSILON® using the coal specification and other technical data common to IEAGHG studies (Appendix D). The power plant (Figure C.1) uses high-pressure and high-temperature steam (295 bar, 600 °C) and has a gross electrical power output of 900 MW. At its design point (full load operation without CO₂ capture), the net efficiency is 44.4%, related to the lower heating value (LHV). The ambient air, which is taken from the inside the boiler building, is split into primary air and secondary air. While the secondary air is sent directly to the boiler, the primary air is used to preheat a feedwater bypass and then used as mill air. A steam preheater is foreseen to increase the air temperature at the air preheater inlet. The flue-gas cleaning incorporates three common cleaning steps:

- deNOx
- electrostatic precipitator
- wet flue gas desulfurisation.

The preheating train consists of five low-pressure preheaters, the de-aerator and three high-pressure preheaters. Just before entering the boiler unit, the feed water is heated to 300 °C. The cooling system is based on a natural draught cooling tower, which supplies cooling water at 16 °C. With a temperature gain in the condenser of 10 K and a temperature approach of 3 K, the condenser pressure is determined to be 40 mbar.

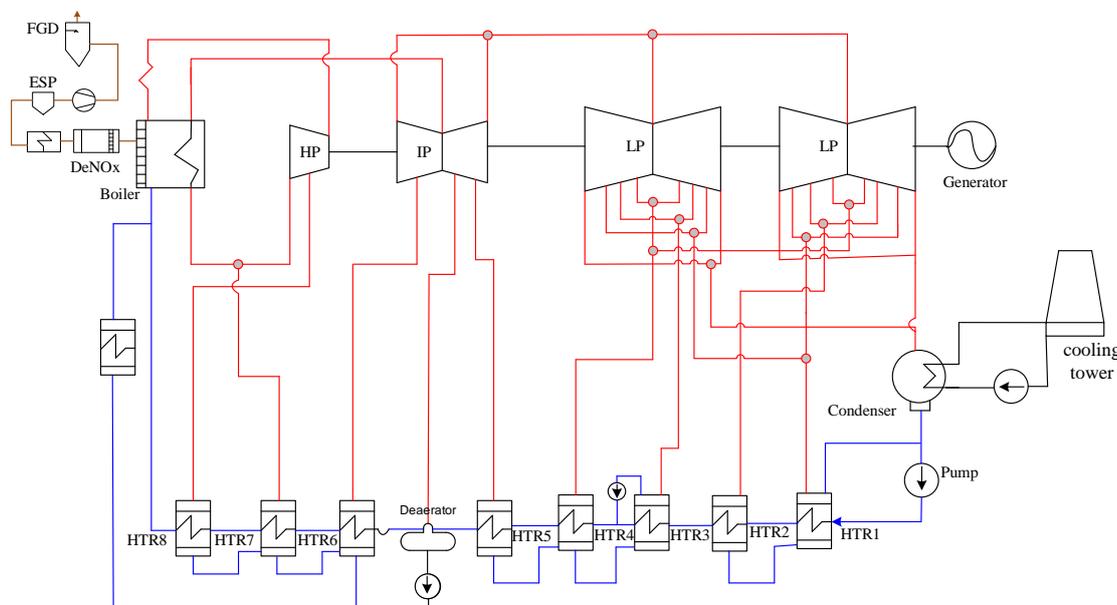


Figure C.1 Process flow diagram for an ultra-supercritical pulverised coal-fired power plant with integrated post-combustion capture process. ESP = electrostatic precipitator; FGD = flue gas desulfurisation; HP = high pressure; HTR = Heater; IP = intermediate pressure; LP = low pressure

The flue gas details after flue gas desulfurisation generated by EBSILON® are shown in Table C.1.

Table C.1 Flue gas details for ultra-supercritical pulverised coal-fired power plant

PARAMETER	VALUE
Flow rate, kg/s	826.8
Temperature, °C	50
Pressure, kPa	101.8
H ₂ O, mol%	12.1
CO ₂ , mol%	13.4
N ₂ , mol%	70.4
Ar and other gases, mol%	0.8
O ₂ , mol%	3.3

In the power plant integrated with the post-combustion CO₂-capture plant, steam needed for the regeneration of the amine solution is extracted from the steam cycle at the cross-over point between the medium and low-pressure turbine, resulting in a reduction of output from the power station. There is no energy recovery from the steam expansion.

C.2 Natural-gas-fired combined-cycle

The performance of a natural-gas-fired combined-cycle was determined using EBSILON® using the natural-gas specification and other technical data common to IEAGHG studies (Appendix D). The natural-gas-fired combined-cycle (Figure C.2) consists of a sequential combustion gas turbine delivering flue gas at high temperature for the subsequent heat-recovery steam generator. The water-steam cycle is a three-pressure-level process (live steam 585 °C, 159 bar) with a reheat (585 °C, 40 bar) and has a gross electrical power output of 883 MW. The cooling system is based on a mechanical draught cooling tower, which supplies cooling water at 19 °C. With a temperature gain in the condenser of 11 K and a temperature approach of 3 K, the condenser pressure is determined to be 45 mbar.

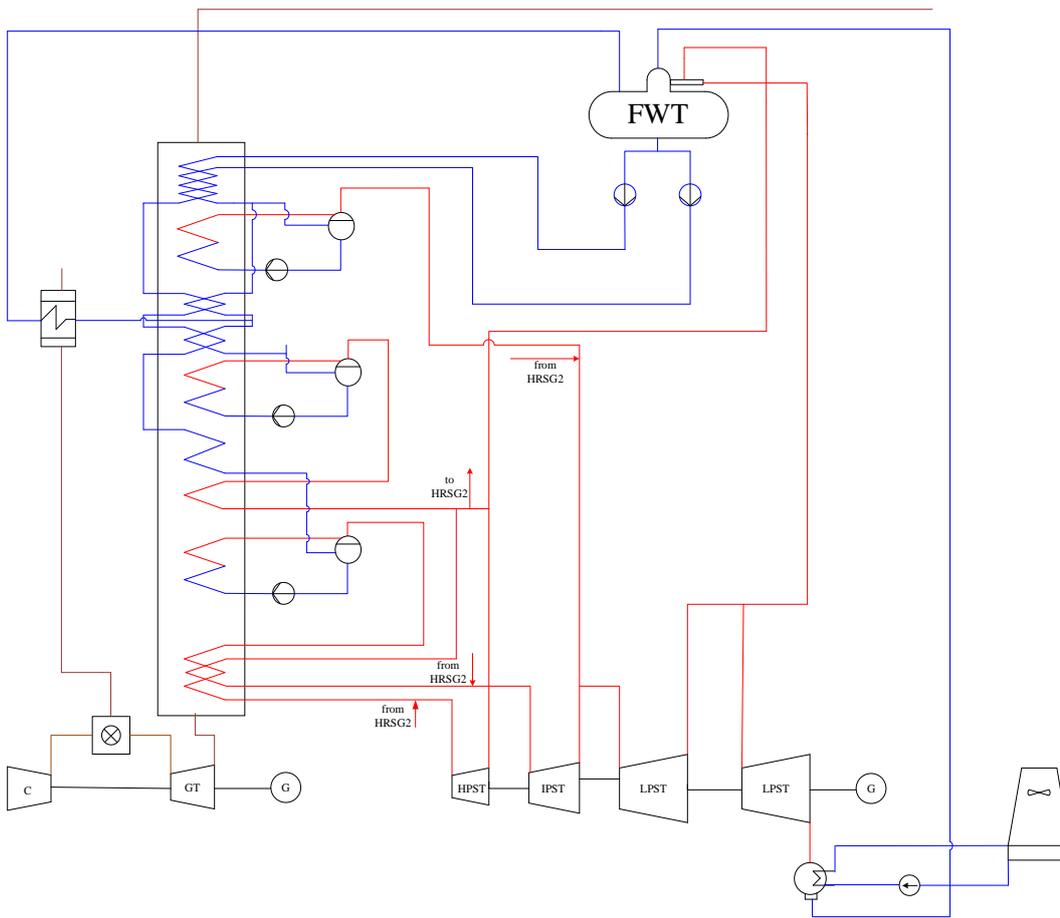


Figure C.2 Process diagram for the natural-gas-fired combined-cycle

The flue gas details generated by EBSILON® after the heat-recovery steam generator are shown in Table C.2.

Table C.2 Flue gas details for natural-gas-fired combined-cycle

PARAMETER	VALUE
Flow rate, kg/s	1320
Temperature, °C	85
Pressure, kPa	101.8
H ₂ O, mol%	8.5
CO ₂ , mol%	4.2
N ₂ , mol%	74.4
Ar and other gases, mol%	0.9
O ₂ , mol%	12.0

In the power plant integrated with the post-combustion CO₂-capture plant, steam needed for the regeneration of the amine solution is extracted from the heat-recovery steam generator at the cross-over point between the medium and low-pressure turbine, resulting in a reduction of output from the power station. Energy is recovered from the steam expansion via a separate let-down turbine.

Appendix D Techno-economic performance of power plants with and without post-combustion CO₂ capture using PZ/AMP

Table D.1 Overview of techno-economic results for power plants with and without post-combustion CO₂ capture (PCC) using piperazine/amino-methyl-propanol (PZ/AMP) (inter-cooling/rich split)

Costs (/1000€) 2015 1st Qtr	Ultra-supercritical coal-fired power plant		Natural gas combined-cycle	
	Power plant	PCC (three process trains)	Power plant	PCC (four process trains)
Capital costs				
Equipment	–	112,165	–	107,442
Materials	–	71,780	–	84,028
Labour	–	19,107	–	22,458
Engineering contractors' fees	–	20,305	–	21,393
Process contingency	–	35,737	–	37,651
Project contingency	–	25,909	–	27,297
Total plant costs	1,222,157	285,004	765,087	300,269
Owners' costs and fees	85,551	19,950	53,556	21,019
Spare parts	6,111	1,425	3,825	1,501
Start-up	28,990	10,309	13,225	18,582
Total capital requirement	1,342,809	316,687	835,693	341,371
Fuel cost				
Coal/natural gas	128,817	128,817	226,519	226,519
Annual fixed operation & maintenance costs				
Operating labour	4,800	5,400	1,800	2,100
Maintenance	18,332	22,662	17,858	24,454
Administrative and support	2,320	2,708	1,397	1,804
Taxes and insurance	1,222	15,108	8,112	11,115
Subtotal	37,674	45,878	29,157	39,473
Annual variable operation & maintenance costs				
Cooling and make-up water	1,624	2,039	852	1,126
Catalyst	3,022	3,022	–	–
Limestone	1,108	1,108	–	–
PZ/AMP	–	7,439	–	3,815
Corrosion inhibitor	–	1,488	–	763
Other chemicals	1,786	2,058	2,560	2,699
Waste disposal	–	633	–	680

Costs (/1000€) 2015 1st Qtr	Ultra-supercritical coal-fired power plant		Natural gas combined-cycle	
	Power plant	PCC (three process trains)	Power plant	PCC (four process trains)
Subtotal	7,540	17,787	3,412	9,083
Economic performance				
LCOE (€/MWh)	51.6	79.5	52.9	73.9
CO ₂ -avoided cost (€/t CO ₂)	–	42.8	–	67.1

Appendix E Data used in this study

The fuel data used in this study, as shown in Table E.1 to E.4, were taken from *Criteria for Technical and Economic Assessment of Plants with Low CO₂ Emissions*, Version C-4, February 2013, provided by the IEAGHG.

Table E.1 Fuel data used in this study

Coal analysis	
Coal type	Eastern Australia, open cast bituminous
Moisture (as received), wt%	9.5
Ash (as received), wt%	12.2
Carbon (dry-ash free), wt%	82.5
Hydrogen (dry-ash free), wt%	5.6
Oxygen (dry-ash free), wt%	8.97
Nitrogen (dry-ash free), wt%	1.8
Sulfur (dry-ash free), wt%	1.1
Chlorine (dry-ash free), wt%	0.03
Higher heating value (as received), MJ/kg	27.06
Lower heating value (as received), MJ/kg	25.87
Hardgrove index	45
Ash analysis, wt%	
SiO ₂	50.0
Al ₂ O ₃	30.0
Fe ₂ O ₃	9.7
CaO	3.9
TiO ₂	2.0
MgO	0.4
Na ₂ O	0.1
K ₂ O	0.1
P ₂ O ₅	1.7
SO ₃	1.7
Ash fusion temperature (reducing), °C	1350
Natural gas analysis	
Methane, vol%	89.0
Ethane, vol%	7.0
Propane, vol%	1.0
Butane, vol%	0.1
Pentane, vol%	0.01

CO ₂ , vol%	2
N ₂ , vol%	0.89
Pressure, MPa	7
Higher heating value, MJ/kg	51.473
Lower heating value, MJ/kg	46.502

Table E.2 Emission limits

Emission limits (solid-fuel combustion)	
SO ₂ , mg/Nm ³ (6% O ₂ combustion)	150 / 50
NO _x , (as NO ₂) mg/Nm ₃ (6% O ₂ combustion)	150 / 10
Particulars, mg/Nm ³ (6% O ₂ combustion)	10 / –

Table E.3 Cooling system parameters

Ambient conditions	
Air temperature (dry-bulb, average), °C	9
Humidity (average), %	80
Pressure (average), kPa	101.3
Cooling system	
Mechanical/natural draught cooling towers	
Cooling-water inlet-outlet, °C	11
Cooling-water approach to wet bulb temperature, °C	7
Turbine condenser minimum ΔT , °C	3

Table E.4 Economic parameters

Total plant cost (TPC)	
Installed costs	Equipment costs + material costs + labour costs
Engineering contractor's fees	10% of installed costs
Project contingency	10% of (installed costs + engineering contractor's fee)
Process contingency (only for carbon capture and storage)	16% of (installed costs + engineering contractor's fee)
Total capital requirement	
Owners costs and fees	7% of TPC
Spare parts	0.5% of TPC
Start-up costs	
Maintenance, operating and support labour costs	3 months
Maintenance materials	1 month
Chemicals, consumables and waste disposal costs	1 month
Fuel cost	25% of 1 month

Modifications	2% of TPC
Construction time	
Pulverised coal and natural gas plants	3 years
Capital expenditure schedule	
Pulverised coal and natural gas plants	20%/45%/35% of TPC, year 1–3
Capacity factor	
All except year 1	85% (7446 h)
Year 1	50% (4380 h)
Discount rate	
Plant construction and operation	8%
Operating life	
Base case	25 years
Fuel prices	
Coal	2.5 €/GJ
Natural gas	5.0 €/GJ
Fixed operating costs	
Maintenance costs	
PC plant	1.5% of TPC/year
NGCC	2.2% of TPC/year
Maintenance materials	60% of maintenance costs
Maintenance labour	40% of maintenance costs
Operating labour cost	60 k€/person-year
Number of operators	
Pulverised coal plant	16
Pulverised coal + CO ₂ capture	18
Natural gas combined-cycle plant	6
Natural gas combined-cycle + CO ₂ capture	7
Number of operating shifts	5
Administrative/support labour	30% of operating labour + 12% of maintenance cost
Insurance cost	0.5% of TPC
Local taxes and fees	0.5% of TPC
Variable operating costs	
Raw process water	0.2 €/m ³
Limestone	20 €/t
Amine	5 €/kg
Corrosion inhibitor	20% of MEA cost
Soda ash	0.56 €/kg
Special waste disposal costs	20.5 €/kg
CO ₂ transport and storage	10 €/t CO ₂ stored (not used in this study)

Abbreviations

AMP	amino-methyl-propanol	FEED	front-end engineering design
ASU	air-separation unit	FGD	flue gas desulfurisation
CA	carbonic anhydrase	GALLM-E	Global and Local Learning Model–Electricity
CAP	Chilled Ammonia Process	GO	graphene–oxide
CAR	ceramic autothermal recovery	GPU	gas permeation unit
CCS	carbon capture and storage	GTI	Gas Technology Institute
c.f.	compared with	HP	high pressure
CFB	circulating fluidised bed	IEAGHG	International Energy Agency Greenhouse Gas Research and Development Programme
CFBC	circulating fluidised-bed combustion	IFPEN	French Petroleum Institute (IFP) Energies Nouvelles
CFM	construction finance multiplier	IGCC	integrated gasification combined-cycle
CLAS	chemical looping air separation	iG-CLC	in-situ gasification chemical-looping combustion
CLC	chemical-looping combustion	LCOE	levelised cost of electricity
CLOU	chemical looping with oxygen uncoupling	LHV	Lower heating value
COE	cost of electricity	MEA	monoethanolamine
CPU	CO ₂ purification unit (also, compression and purification unit)	MDEA	methyl-diethanolamine
CSIC	Spanish National Research Council	MHI	Mitsubishi Heavy Industries
CSIRO	Commonwealth Scientific and Industrial Research Organisation	MOF	metal organic framework
DAC	direct air capture	MTR	Membrane Technology and Research Inc.
DEA	diethanolamine	NCCC	National Carbon Capture Center
DOE	Department of Energy	NETL	National Energy Technology Laboratory
EOR	enhanced oil recovery	NGCC	Natural gas combined-cycle
EPRI	Electric Power Research Institute	NO _x	Nitrogen oxides (NO, NO ₂ , N ₂ O)
ESA	electrical swing adsorption		
EU	European Union		

NTNU	Norwegian University of Science and Technology	SCPC	supercritical pulverised coal
OC	oxygen carrier	SPOC	staged pressurised oxyfuel combustion
O&M	operations & maintenance	SRD	specific reboiler duty (GJ/tCO ₂ , MJ/kgCO ₂)
PCC	post-combustion capture of CO ₂	TBAB	tert-n-butylammonium bromide
PDMS	poly dimethyl siloxane	TBAF	tetra-n-butyl ammonium fluoride
PEEK	polyether ether ketone	TCM	Technology Centre Mongstad
PEI	polyethyleneimine	TNO	Netherlands Organisation for Applied Scientific Research
PSA	pressure swing adsorption	TRL	technology readiness level
PZ	piperazine	TSA	temperature swing adsorption
RTI	Research Triangle Institute	USCPC	ultra-supercritical pulverised coal
sCO ₂	supercritical CO ₂	VPSA	vacuum pressure swing adsorption
SEWGS	sorbent-enhanced water–gas shift	WGS	water–gas shift
SO _x	sulfur oxides (SO ₂ , SO ₃)		

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